

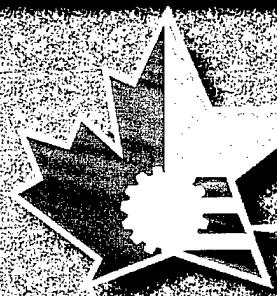
# Ion Beam Processing (IBP) Technologies

## *Sector Study*

An  
Assessment of  
IBP  
Technologies, Trends  
and  
Applications

DISSEMINATION STATEMENT A  
Approved for public release  
Distribution Unlimited

June 1996



N A T O

North American Technology and Industrial Base Organization

DTIC QUALITY INSPECTED

*Collaborative Virtual Prototyping Study*

**PLEASE CHECK THE APPROPRIATE BLOCK BELOW:**

-AO #



copies are being forwarded. Indicate whether Statement A, B, C, D, E, F, or X applies.



**DISTRIBUTION STATEMENT A:**

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED



**DISTRIBUTION STATEMENT B:**

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES ONLY: (Indicate Reason and Date). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office).



**DISTRIBUTION STATEMENT C:**

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND THEIR CONTRACTORS: (Indicate Reason and Date). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office).



**DISTRIBUTION STATEMENT D:**

DISTRIBUTION AUTHORIZED TO DoD AND U.S. DoD CONTRACTORS ONLY: (Indicate Reason and Date). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office).



**DISTRIBUTION STATEMENT E:**

DISTRIBUTION AUTHORIZED TO DoD COMPONENTS ONLY: (Indicate Reason and Date). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office).



**DISTRIBUTION STATEMENT F:**

FURTHER DISSEMINATION ONLY AS DIRECTED BY (Indicate Controlling DoD Office and Date) or HIGHER DoD AUTHORITY.



**DISTRIBUTION STATEMENT X:**

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND PRIVATE INDIVIDUALS OR ENTERPRISES ELIGIBLE TO OBTAIN EXPORT-CONTROLLED TECHNICAL DATA IN ACCORDANCE WITH DoD DIRECTIVE 5230.25, WITHHOLDING OF UNCLASSIFIED TECHNICAL DATA FROM PUBLIC DISCLOSURE, 6 Nov 1984 (Indicate date of determination). CONTROLLING DoD OFFICE IS (Indicate Controlling DoD Office).



This document was previously forwarded to DTIC on \_\_\_\_\_ (date) and the AD number is \_\_\_\_\_.



In accordance with provisions of DoD instructions, the document requested is not supplied because:



It will be published at a later date. (Enter approximate date, if known).



Other. (Give Reason)

DoD Directive 5230.24, "Distribution Statements on Technical Documents," 18 Mar 87, contains seven distribution statements, as described briefly above. Technical Documents must be assigned distribution statements.

*Ron Cox*

*Bob Stillings*  
Print or Type Name

*J. S. J.*  
Authorized Signature/Date

*703 604 6200*  
Telephone Number

# **Ion Beam Processing (IBP) Technologies**

## **Sector Study**

### **FINAL REPORT**

**Prepared for the North American Technology  
and Industrial Base Organization (NATIBO)**

**Prepared by BDM Federal, Inc.**

**June 1996**

**19970314 099**

## **FOREWORD**

In March 1995, the North American Technology and Industrial Base Organization's (NATIBO) Steering Committee commissioned a study of ion beam processing (IBP) technologies applications and their implementation throughout North America's defense and commercial industrial bases.

This report provides the results of the study of IBP applications and implementation conducted between April 1995 and May 1996. It highlights the current state of the technology, and identifies and examines technical and socio-economic barriers and facilitators to implementation, as well as potential dual-use applications of IBP technologies. In addition, it recommends cultural conditions that need to be fostered and steps that need to be taken to ensure the adoption and the effective widespread use of IBP technologies in support of the military and civilian industrial sectors.

This report was prepared by BDM Federal, Inc. (BDM), 1501 BDM Way, McLean, VA 22102 for NATIBO under contract number DAAA08-91-D-0008. Ed Dorchak managed the study. Principal investigators and authors of the report were Michael Brown, Mel Hafer, and Mark Priest.

## ACKNOWLEDGMENTS

The authors would like to express their appreciation to the many individuals whose cooperation in providing essential information made this effort possible. This study could not have been completed without the dedicated efforts of the IBP Working Group members, listed here in alphabetical order:

Mr. Luis E. Garcia-Baco	Army Acquisition Pollution Prevention Support Office, Headquarters, U.S. Army Materiel Command Principal Investigator
Ms. Cynthia Gonsalves	Dual Use Technology Policy and Programs, Office of Secretary of Defense for Economic Security
Ms. Sylvia Jeffrey	Office of the Director, General International and Industry Programs, Canadian Department of National Defense
Mr. Bryan Prosser	Program Support Directorate, Marine Corps Systems Command
Mr. Dilip Punatar	Advanced Industrial Practices Division, Manufacturing Technology Directorate, Wright Laboratories
Mr. Michael Slack	Office of the Director, General International and Industry Programs, Canadian Department of National Defense
Mr. Rod White	U.S. Army Industrial Engineering Activity

The authors would also like to express their appreciation to the many companies, government agencies and academic institutions who supplied us with timely, important information necessary to conduct this assessment:

- Acadian Platers
- Active Metal/Bristol Plating
- Albany Marine Corps Depot
- Army Research Lab
- Boeing Corporation
- Cametoid Advanced Technologies
- Chrysler
- Coatings 85
- Corpus Christi Army Depot
- Dr. Don Mattox (SVC/Sandia)
- Eaton Corporation
- Empire Hard Chrome
- Ford
- General Motors R&D Center
- Hughes Research Lab
- Husky Injection Molding
- Implant Sciences Corp.
- ISM Technologies
- Lawrence Berkeley Lab
- Lawrence Livermore Lab
- Los Alamos National Lab
- NDCEE/CTC
- Naval Research Lab
- North Island Naval Aviation Depot
- Northstar Research
- Northwestern University/BIRL
- Oak Ridge National Lab
- Pure Coatings, Inc.
- Ralph Alexander
- Simon Fraser University
- SK Handtools
- Southwestern Research Institute
- Spire Corporation
- Torcad/DC Chrome
- Wastewater Technology Center

## **DISCLAIMER**

The mention of specific products or companies does not constitute an endorsement by BDM, the U.S. Government, or the Canadian Government. Use of the information contained in this publication shall be with the user's understanding that neither BDM nor the two Governments, by the inclusion or exclusion of any company in this document, provides any endorsement or opinion as to the included or excluded companies' products, capabilities, or competencies. The list of companies contained in this document is not represented to be complete or all inclusive.

## TABLE OF CONTENTS

FOREWORD .....	iii
ACKNOWLEDGMENTS.....	v
DISCLAIMER .....	vii
TABLE OF CONTENTS.....	ix
LIST OF FIGURES .....	xi
LIST OF TABLES .....	xi
EXECUTIVE SUMMARY.....	ES-1
1.0    INTRODUCTION .....	1
1.1    Background.....	1
1.2    Purpose .....	1
1.3    Objectives .....	1
1.4    Scope .....	2
1.5    Methodology.....	2
1.6    Report Structure.....	3
2.0    TECHNOLOGY OVERVIEW .....	5
2.1    Ion Beam Processing Technologies in the Context of Other Metal Finishing Technologies .....	5
2.2    Ion Implantation.....	7
2.3    Ion Beam Assisted Deposition.....	14
3.0    IBP INDUSTRY DEMOGRAPHICS .....	17
3.1    IBP Companies .....	17
3.2    Government IBP Technology Researchers .....	30
3.3    Academic IBP Technology Researchers .....	41
3.4    International .....	45
4.0    APPLICATIONS OF IBP TECHNOLOGIES .....	51
4.1    Ion Implantation Applications .....	52
4.2    Ion Beam Assisted Deposition (IBAD) .....	59
5.0    BENEFITS OF IBP TECHNOLOGIES .....	63
5.1    Benefits of Mass Analyzed and Direct Ion Implantation .....	63
5.2    Additional Benefits of Plasma Source Ion Implantation .....	67
5.3    Benefits of Ion Beam Assisted Deposition .....	68
6.0    BARRIERS TO COMMERCIALIZATION.....	71
6.1    Socio-Economic or Market Barriers .....	71
6.2    Technical Barriers.....	75
7.0    CONCLUSIONS .....	79
7.1    Ion Implantation is a Mature, Environmentally Safe Process .....	79
7.2    Plasma Source Ion Implantation and IBAD Require Additional Study and Demonstration.....	79
7.3    IBP Technologies Have Not Achieved Wide Acceptance for Metal Surface Finishing Applications in North America .....	70
7.4    Direct Ion Implantation of Nitrogen and Metal Ions are Technologies that are Ready NOW for Metal Surface Finishing Applications .....	80
7.5    Far Eastern, Russian and European Markets are Currently the Most Viable Markets for IBP Technologies .....	80
7.6    The Financial Investment for IBP Technologies is Presently Considerable and Risky .....	81

## TABLE OF CONTENTS (CONTINUED)

8.0	RECOMMENDATIONS.....	83
8.1	Develop Additional IBP Metal Surface Finishing Capabilities within the DOD and DND Sustainment Communities .....	83
8.2	Develop a Near-Term IBP Technology Insertion Program .....	84
8.3	Ensure Adequate Funding and Management Oversight of IBP R&D Efforts to Overcome Technical Barriers.....	84
8.4	Sponsor Education Activities.....	84
8.5	Organize a Multilateral, Multiservice IBP Technology Working Group with DOD and DND Co-Chairs .....	85
8.6	Collaborate with a Professional or Technical Organization or Both to Explore Possible Commercial IBP Technology Standard Development.....	85
8.7	Develop an Outreach Program to Specifically Educate and Inform Small Businesses .....	85
8.8	Establish Memoranda of Understanding (MoUs) with Foreign Countries.....	86
8.9	Collect and Validate Cost Data.....	86
Appendix A	Acronyms.....	A-1
Appendix B	Bibliography .....	B-1
Appendix C	Points of Contact .....	C-1
Appendix D	IBP International Industry Demographics .....	D-1
Appendix E	Successful IBP Technology Demonstrations.....	E-1
Appendix F	Environmental Costs Not Incurred In The Use of IBP Technologies	F-1

## LIST OF FIGURES

1-1	IBP Technology Study Methodology.....	3
2-1	Mass Analyzed Ion Implantation System Schematic .....	11
2-2	Direct Ion Implantation System Schematic .....	12
2-3	Plasma Source Ion Implantation System Schematic .....	12
2-4	IBAD System Schematic.....	15

## LIST OF TABLES

ES-1	IBP Technology Companies .....	ES-2
ES-2	Government IBP Technology Researchers .....	ES-3
ES-3	Academic IBP Technology Researchers .....	ES-3
ES-4	Current and Demonstrated Potential IBP Technology Applications.....	ES-4
2-1	Metal Surface Finishing Techniques.....	6
2-2	History of IBP Technology Development.....	8
2-3	Surface Properties Modified by Different Ion Species .....	9
3-1	IBP Capabilities of Companies .....	17
3-2	Capabilities of the Government IBP Technology Researchers .....	31
3-3	U.S. Army IBP R&D Projects .....	32
3-4	U.S. Navy IBP R&D Projects .....	33
3-5	Capabilities of Academic IBP Technology Researchers.....	41
3-6	Capabilities of Other North American Academic IBP Technology Researchers .....	45
4-1	Current and Demonstrated Potential IBP Technology Applications.....	52

## EXECUTIVE SUMMARY

### ES.1 Introduction

The purpose of this NATIBO study was to assess the maturity, level of use, utility, and viability of ion beam processing (IBP) technologies for metal surface finishing applications. Over the past decade, ion implantation, the most visible IBP technology, has been able to find a technical and commercial niche improving the wear properties of medical devices such as titanium hip and knee joints. Ion implantation has also been widely used in the semiconductor industry sector for more than thirty years to provide precise control of semiconductor wafer manufacturing. However, IBP technologies have not been able to successfully penetrate other North American metal surface finishing markets despite successful demonstrations in many applications.

The objectives of the study were:

- Identify the status of IBP technology development,
- Identify current and potential application areas,
- Identify the benefits of IBP technologies,
- Identify current defense and commercial activities related to IBP technology development and use,
- Identify limitations and barriers to IBP technology use, and
- Recommend actions for government and industry to fully capitalize on the potential of IBP technologies in the metal surface finishing industry sector.

This study encompassed the collection and analysis of technical, business, and policy information related to IBP research efforts and industrial capabilities in both the U.S. and Canada. Additional information on foreign research efforts and capabilities was collected and analyzed where possible. The IBP technologies investigated and analyzed in this study were:

- Mass analyzed ion implantation, the technique used in semiconductor manufacturing;
- Direct nitrogen ion implantation;
- Direct metal ion implantation;
- Plasma source ion implantation (PSII); and,
- Ion beam assisted deposition (IBAD).

NATIBO initially selected IBP technologies to study under this program because of the environmental benefits offered by these technologies as potential alternatives or enhancements to cadmium and chromium

electroplating. As the study evolved, though, the study team recognized that the IBP technologies have broader application in the metal surface finishing industrial sector and the focus of the effort was modified accordingly. The environmental benefits of the technologies were still considered, but in the larger context of solving troubling metal surface finishing problems.

## ES.2 Demographics

Companies, U.S. and Canadian Government researchers, and academic researchers were considered in this study.

### ES.2.1 Companies

Companies involved in studying and advancing IBP technologies include those companies which provide and manufacture the equipment used in the process of IBP, and those actually involved in applying these technologies to various applications. Table ES-1 illustrates the key industry players in the IBP technologies area for metal surface finishing and their areas of concentration and study.

Table ES-1. IBP Technology Companies

Company	Hardware Provider	Service Provider	Researcher	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD
Beamalloy		X	X	X			X
Boeing			X			X	X
Eaton Corp.	X		X			X	
Empire Hard Chrome		X	X			X	
Epion Corp.	X	X	X	X	X		X
GM R&D Center		X	X			X	
Hughes Research Lab		X	X			X	
Implant Sciences	X	X	X	X	X		X
ISM Technologies	X	X	X		X		X
NDCEE							
Spire Corp.	X	X	X	X		X	X
Southwest Research Institute		X	X	X	X		X

### ES.2.2 Government Researchers

Government researchers involved in studying and advancing IBP technologies include laboratories and depots within the U.S. Department of Defense (DOD) and the Canadian Department of National Defence (DND). The U.S Department of Energy (DOE) National Labs also have substantial programs on IBP

technology research and equipment development as a result of the fusion and space weapons programs. The Advanced Research Projects Agency (ARPA) and the U.S Environmental Protection Agency sponsor research to evaluate alternatives to pollution causing metal finishing techniques such as cadmium and chromium electroplating. Table ES-2 provides a snapshot view of these government players and their IBP technology areas of research.

**Table ES-2. Government IBP Technology Researchers**

Agency	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
<b>DoD</b>					
ARL	X			X	X <sup>2,3</sup>
ARPA					X <sup>4</sup>
CCAD	X				X <sup>1</sup>
NRL	X			X	X <sup>2,3</sup>
Wright Lab				X	
<b>DOE</b>					
LBL		X			
LLL	X				
LANL			X		
ORNL	X			X	
<b>Other</b>					
EPA					X <sup>4</sup>

<sup>1</sup> Electroplating

<sup>2</sup> Ion beam mixing

<sup>3</sup> Semiconductor ion implantation

<sup>4</sup> Proponent

### ES.2.3 Academic Researchers

Academic researchers within the U.S. and Canada are actively involved in further understanding the basic science of IBP technologies. Table ES-3 provides a summary of the most prominent academic IBP researchers.

**Table ES-3. Academic IBP Technology Researchers**

Academic Researcher	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
BIRL/ Northwestern	X			X	X <sup>1,2</sup>
INRS-Montreal			X		
University of Tennessee			X		
Univ. of Wisconsin	X		X	X	X <sup>1,2</sup>

<sup>1</sup> Ion Beam Mixing

<sup>2</sup> Semiconductor ion implantation

### ES.3 Applications

The largest current metal finishing application of IBP technologies is in the medical industry sector. Mass analyzed ion implantation is typically used to implant nitrogen into a number of medical devices to improve wear resistance, and thereby increase life expectancy of the medical implant. Examples of the ion implanted devices include hip replacements, knee joints, shoulder implants, spinal screws, and dental implants. Industry experts estimate that in excess of 100,000 components are ion implanted each year.

IBP technologies have been demonstrated in many other application areas, including the aerospace, automotive, and cutting tool areas. Table ES-4 summarizes the example applications for IBP technologies in these areas, as well as the medical area. The documented successes of IBP technologies in these application areas warrant further consideration.

**Table ES-4. Current and Demonstrated Potential Ion Beam Technology Applications**

Application Area	Example Applications	Current	Demonstrated Potential	IBP Technology	Competing Technology
Medical	hip replacements, knee joints, shoulder implants, spinal screws, dental implants, optical filters, X-ray mirrors	X	X	nitrogen ion implantation, IBAD	chemical vapor deposition, physical vapor deposition,
Aerospace	ball bearings, hinge pin bearings, gear box bearings, gears, pillow blocks, turbine blades, turbine vanes		X	nitrogen ion implantation, IBAD	thermal spray, ion plating
Automotive	cylinder liners, piston rings, cam shafts, cam followers		X	nitrogen ion implantation	thermal spray, sputtering
Tools and Dies	cutting tools, punches, tool inserts, knives	X	X	nitrogen ion implantation, metal ion implantation	chemical vapor deposition, physical vapor deposition,
Non-metallic Materials	ceramic internal combustion engine components, plastics, glass		X	metal ion implantation, IBAD	

### ES.4 Benefits of IBP Technologies

The are many benefits to using mass-analyzed and direct ion implantation for metal surface finishing. These benefits are:

- Ion implantation is an environmentally acceptable metal surface treatment process;
- Ion implantation processing costs are decreasing;

- Surface properties such as wear resistance and corrosion resistance of implanted parts are improved;
- Surface properties of parts can be tailored without adversely affecting bulk properties;
- Ion implantation is a comparatively low temperature process;
- Since ion implantation is not a coating process there is no possibility of a coating delaminating;
- Ion implantation is a highly controllable and reproducible process, as evidenced in the semiconductor industry;
- Ion implantation does not change the dimensions of implanted parts;
- Implanted parts do not require any additional rework;
- Virtually any element in the periodic table can be implanted; and,
- Ion implanted parts are biocompatible.

In addition to the above benefits, there are also advantages specific to the use of PSII. These benefits are:

- PSII allows non-line-of-sight processing;
- Workpiece manipulation is not required; and,
- PSII promises faster throughput than either mass-analyzed or direct ion implantation.

IBAD is a hybrid of ion implantation and physical vapor deposition. It combines the advantages of both techniques. These benefits are:

- IBAD is a comparatively low temperature process like ion implantation;
- IBAD coatings exhibit high adhesion;
- There is no inherent coating thickness limitation;
- IBAD coatings exhibit higher density than traditional coatings such as electroplated coatings;
- IBAD is a highly reproducible process; and,
- IBAD allows precise modulation of composition with depth, allowing the development of exotic coatings.

## **ES.5 Barriers to Commercialization**

Two types of barriers to commercialization were discovered for IBP technologies: socio-economic barriers and technical barriers.

### **ES.5.1 Socio Economic Barriers**

From a socio-economic and market perspective, the primary barriers are related to the current financial burden associated with acquiring and operating IBP equipment, and the nature of the technologies. Other barriers are based upon perceptions that were fostered during the initial commercialization of the IBP technologies in the 1980's. The specific barriers are as follows:

- IBP technologies require high capital investment cost;
- IBP technologies processing costs are high compared to traditional techniques such as electroplating;
- IBP technologies have higher labor costs than traditional metal surface finishing techniques;
- IBP technologies are thought to be harmful, and difficult to understand and implement;
- The continued development of low-cost environmental remediation techniques for traditional metal surface finishing techniques;
- Market conservatism;
- Conflicting production priorities; and,
- Need for specification changes in order to implement IBP technologies.

### **ES.5.2 Technical Barriers**

The technical barriers to the commercialization of IBP technologies are directly related to the physical limitations of the IBP processes and equipment, and the present gaps in knowledge regarding the physics of the implantation process. The specific technical barriers are:

- With the exception of PSII, IBP technologies are line of sight processes;
- Size of vacuum chambers limits the size of pieces that can be treated;
- Wear and corrosion testing is difficult;
- Implantation non-uniformity;
- Shallow penetration depth of the implant;
- Lack of knowledge of optimum ion implantation parameters; and,
- Lack of understanding of implantation mechanisms that improve wear or corrosion resistance.

### **ES.6 Conclusions**

The conclusions are of this study are based on observations of the current technical and business environment associated with the IBP technologies. The specific conclusions of this study are as follows:

- Ion implantation is a mature, environmentally safe process;
- Ion implantation has a niche in the medical device industry sector;
- PSII and IBAD are less mature technologies and therefore require additional study;
- IBP technologies have not achieved wide acceptance for metal surface finishing applications in North America;
- IBP technologies have potentially high dual-use applicability;

- Direct ion implantation of nitrogen and metal ions are technologies that have been demonstrated and are ready for metal surface finishing applications;
- Far Eastern, Russian and European markets are the most viable current markets for IBP technologies;
- Japan has invested heavily in IBP technologies through the Advanced Material Processing and Machining Technology Research Association (AMMTRA) program; and,
- Financial investment for IBP technologies is both considerable and risky.

#### **ES.7 Recommendations**

The recommendations resulting from this study are designed to overcome the market and technical barriers to commercialization and address appropriate conclusions presented above. The recommendations define specific actions that could be undertaken to foster the advancement and successful incorporation of IBP technologies, and ensure the dual-use of these technologies within the North American commercial and defense industrial bases. The specific recommendations of this study are:

- Develop additional IBP metal surface finishing capabilities with DOD and DND sustainment communities;
- Develop a near-term IBP technology insertion program to highlight potential of IBP technologies;
- Ensure adequate funding and management oversight of IBP R&D efforts to overcome the technical barriers;
- Sponsor education activities such as workshops and conferences;
- Organize a multilateral, multiservice IBP Technology Working Group with DOD and DND Co-Chairs;
- Collaborate with a professional/technical organization to explore possible commercial IBP technology standard development;
- Develop an outreach program to educate and inform small businesses of the benefits of IBP technologies; and,
- Establish Memoranda of Understanding (MOUs) with foreign countries to facilitate joint technology development.
- Collect and validate cost data to permit valid comparison of the IBP costs with other metal surface finishing techniques;

## **1.0 INTRODUCTION**

### **1.1 Background**

The North American Technology and Industrial Base Organization (NATIBO) is chartered to facilitate cooperative technology and industrial base planning and program development among the U.S. Military Services and Canada. To further this mission, the NATIBO has spearheaded an effort to address the challenges of advancing and maintaining technological superiority in light of reduced government research and development funding. The criteria used for selecting technologies to study through this program are:

- the candidate is a key technology area of high interest,
- there is potential for both military and commercial application,
- development and/or production exists in both the U.S. and Canada, and
- there is a good window of opportunity for investment and application.

Through this initiative, common areas of interest are assessed jointly, allowing participating organizations to capture the information they need cost effectively, avoid duplication of effort, and capitalize on scarce resources.

### **1.2 Purpose**

The purpose of this study is to assess the maturity, level of use, utility, and viability of ion

beam processing (IBP) technologies for metal surface finishing applications. Over the past decade, ion implantation, the most visible IBP technology, has been able to find a technical and commercial niche improving the wear properties of medical devices such as titanium hip and knee joints. However, IBP technologies have not been able to successfully penetrate other North American markets despite successful demonstrations in many applications.

This report investigates IBP technologies from technological, cultural, policy, financial, and effectiveness points of view and develops conclusions regarding the status of IBP technologies from each of these perspectives. Recommendations regarding actions that the defense community might consider in response to these conclusions are also presented.

### **1.3 Objectives**

This study identifies and assesses the maturity and applicability of IBP technologies to solve many metal surface finishing problems found in the North American industrial base.

The objectives of the study are to:

- Identify the status of IBP technology development,
- Identify current and potential application areas,
- Identify the benefits of IBP technologies,

- Identify current defense and commercial activities related to IBP technology development and use,
- Identify limitations and barriers to IBP technology use, and
- Recommend actions for government and industry to fully capitalize on the potential of IBP technologies in the metal surface finishing industry sector.

This report describes the current status of IBP technologies and future trends. The report also explores the military and commercial applications of these technologies and the transfer of the technologies among government organizations and between government and private industry. Major government, industry and academia players in the technologies are identified and advantages and limitations of these technologies are discussed and analyzed. From this analysis, conclusions regarding IBP technologies and their further commercialization are discussed in Section 7.0. The recommendations addressing these conclusions are also provided for potential future action in Section 8.0.

#### 1.4 Scope

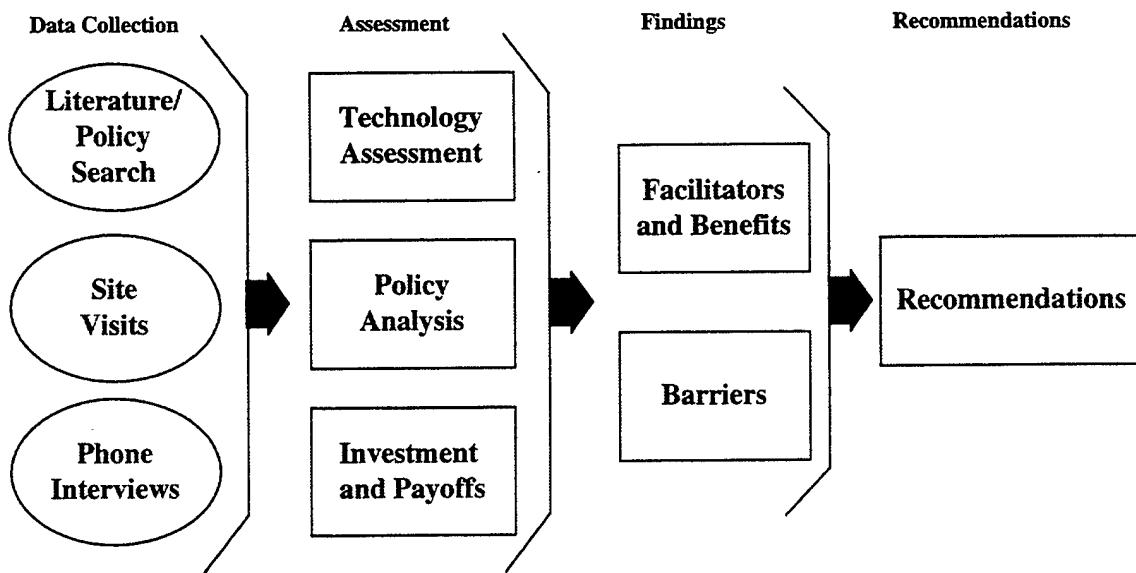
This study encompasses the collection and analysis of technical, business, and policy information related to IBP research efforts and industrial capabilities in both the U.S. and Canada. Additional information on foreign research efforts and capabilities was collected and analyzed where possible. The two IBP

technologies investigated and analyzed in this study are ion implantation and ion beam assisted deposition (IBAD).

The NATIBO initially selected IBP technologies to study under this program because of the environmental benefits offered by these technologies as potential alternatives or enhancements to cadmium and chromium electroplating. As the study evolved, though, the study team recognized that the IBP technologies have broader application in the metal surface finishing industrial sector and the focus of the effort was modified accordingly. The environmental benefits of the technologies are still discussed, but in the larger context of solving troubling metal surface finishing problems.

#### 1.5 Methodology

The IBP technology study required a clear, concise, and well-defined methodology to survey industry effectively and compile military, commercial, political and academic perspectives. The data collected and analyzed for this study were drawn from previously published reports, conference proceedings, journal articles, Internet home pages and other online sources, and discussions with US and Canadian representatives from industry, government and academia. The methodology employed is depicted in Figure 1-1.



**Figure 1-1. IBP Technology Study Methodology.**

The study group's goal was to meet with a representative sample of IBP and metal finishing technology researchers, service and equipment providers, end users, proponents and policy makers. Factors taken into consideration in selecting sites to visit included volume and business with the individual Services and with industry, industrial sector involved, market niche, state of the technology, applications, and new technology development. Site visits were conducted in seven regional areas: Canada (twice), Midwest, Boston, Southwest, Southeast and West Coast.

When it was determined that an industry, university, or government site would not be visited, an extensive phone interview was conducted. Data collection guidelines were developed and used to facilitate obtaining data from all points of contact either through telephone interviews and/or site visits.

Data collected from relevant documents, World Wide Web sites, site visits, and phone interviews were analyzed and incorporated into key sections of this report: technology overview, applications, technology benefits, demographics, technology limitations, conclusions, and recommendations. This report functioned as a working document throughout the data collection and analysis phases of this study.

## 1.6 Report Structure

Section 2.0 of this report provides technical background and descriptions of IBP technologies. Basic metal finishing techniques are first reviewed to provide a context for discussing IBP technologies for metal finishing applications. The technical aspects of ion implantation and IBAD processes are then described.

Section 3.0 presents an overview of the commercial, government and academia entities

currently active in the IBP technology field. Emphasis is on the North American sector but foreign entities are also discussed.

Section 4.0 describes current and potential applications of ion implantation and IBAD with an emphasis on metal finishing applications. Both military and commercial applications are considered.

Section 5.0 summarizes benefits of the IBP technologies. The purpose of this section is to succinctly combine elements of sections 2.0, 3.0 and 4.0 to reinforce the potential of IBP technologies to solve many metal finishing problems.

Section 6.0 describes barriers limiting the commercialization of IBP technologies.

Section 7.0 presents general conclusions of the report.

Section 8.0 provides specific recommendations for addressing the barriers and conclusions discussed in sections 6.0 and 7.0.

Helpful appendices are also provided to assist in the reading of the report, and to expand on results that are summarized in the body of the report.

## **2.0 TECHNOLOGY OVERVIEW**

The purpose of this chapter is to present a brief technical context and overview of the two IBP technologies of interest to this report: ion implantation and ion beam assisted deposition (IBAD). Other metal finishing techniques are presented and discussed as appropriate. The intent is to provide the reader enough technical information to understand the technical content of the remainder of the report. It is not the intent to provide an exhaustive overview of the IBP technologies or other metal finishing technologies.

### **2.1 Ion Beam Processing Technologies in the Context of Other Metal Finishing Technologies**

Metal finishing technologies include a broad spectrum of coating and surface modification techniques. Table 2-1 illustrates the variety of metal finishing techniques used today. Many of the techniques serve the same applications and provide similar performance properties. Table 2-1 first summarizes techniques that are relatively simple and inexpensive to implement, and are readily available commercially. Electroplating falls into this category. Then the table summarizes techniques that are more complicated in terms of equipment requirements and that may also have high temperature and/or vacuum requirements. Finally, the table summarizes techniques that require still more complex and specialized equipment. The techniques in the latter two categories are typically more expensive to implement compared

to the simple techniques because of these additional equipment requirements. Ion implantation and IBAD fall into the last of the three categories.

Presently, the metallic coating and finishing industry is re-evaluating many of the current techniques shown in Table 2-1 in an effort to prevent pollution, and reduce, minimize or eliminate hazardous waste generation. This re-evaluation is being driven by the need to comply with numerous regulatory statutes, including the Clean Water Act (CWA), the Clean Air Act Amendments of 1990 (CAA), the Resource Conservation and Recovery Act (RCRA), and the Canadian Environmental Protection Act, among others. CWA Titles III (standards and enforcement) and IV (permits and licenses) are of particular interest to metal finishers because they outline the regulation of wastewater pollutant discharges. Air emissions are primarily governed by Titles III and IV of the CAA. Title III covers air emissions of hazardous air pollutants such as cadmium, chromium, and lead. Title IV pertains to the phase-out of ozone depleting chemicals (ODCs) that have historically been used for cleaning and pretreating prior to metal coating or finishing. The RCRA provides for the management, treatment, and disposal of hazardous waste and mandates hazardous waste tracking. Additionally, workplace regulations originating from the Occupational Safety and Health Administration (OSHA) are becoming increasingly stringent in the amounts toxic metals

**Table 2-1. Metal Surface Finishing Techniques**

Type Of Process	Process	Substrate	Relative Cost	Environ. Concerns	Applications	Coating Types
Simple	Anodizing	Al, Mg, Zn, Be, Ti, Zr, Th, Stainless Steel	Low	Disposal of chromates and phosphates	Corrosion resistance for aircraft and architectural hardware; decorative, electrical insulation	Oxides of metals
	Chemical Conversion	Fe, steels, Cd, Al, Zn, Mg and their alloys	Low	Solvent Emissions, polluted waters, disposal of heavy metals, chromates	Pre-paint treatment; electrical resistance, decorative	Oxides, manganates, molybdenates, phosphates, and chromates
	Electroplating	Fe, Mg, steels, Zn, Cu, and Ni alloys; ceramics; plastics	Low	Solvent emissions, toxic acid mists, polluted waters, sludges containing toxic metals	Contact, wear, and corrosion resistance; decorative; electrical conductivity	Metals
	Electroless Plating	Metals, ceramics, semiconductors	Moderate	Hazardous vapor treatment, disposal of waste sludge,	Contact, wear, and corrosion resistance; decorative; electrical conductivity	Metals
	Mechanical Plating	Ferrous metals, Cu and its alloys	Low	Residual metals inc. Al, Cd, Cr, Zn; solid waste, polluted waters	Corrosion resistance	Malleable metals
Complex	Cladding	Metals	Low to Moderate	Disposal of cleaning solvents; solvent emissions	Decorative properties; wear and corrosion resistance; increased hardness	Metals
	Detonation Gun	Metals	High	Noxious emission; solvent emissions; metal fumes; noise	Corrosion, oxidation, and abrasion resistance; cathodic, EM and RF protection; electrical and thermal properties	Tungsten carbide, chromium carbide, aluminum oxide
	High Velocity Oxygen Fuel	Metals, some ferrous alloys	Moderate	Possible use of CFC cleaning solvents; noise; combustion gases	Corrosion and wear resistance on machine and aircraft parts	Metals, ceramics
	Plasma Arc	Metals, some ferrous alloys	High	Possible use of CFC cleaning solvents; noise; metal fumes and overspray	Corrosion resistance of small precision parts	Metals
	Vacuum /Plasma	Metals	Moderate to High	Solvent emissions; fumes and overspray may contain toxic metals; ozone; noise	Corrosion, oxidation, and abrasion resistance; cathodic, EM and RF protection; electrical and thermal properties	Tungsten carbide, chromium carbide, aluminum oxide
	Wire Arc	Metals, papers, plastics	Low	Solvent emission; metal fumes; Overspray may contain toxic metals	Corrosion, oxidation, and abrasion resistance; cathodic, EM and RF protection; electrical and thermal properties	Cu, Zn, Al, ferrous alloys

**Table 2-1. Metal Surface Finishing Techniques (continued)**

Type Of Process	Process	Substrate	Relative Cost	Environ. Concerns	Applications	Coating Types
Very Complex	Chemical Vapor Deposition	Metals, plastics, ceramics	Moderate to High	Solvent emissions; corrosive chemicals in traps; potentially toxic vapors	High density, purity and strength; oxidation, corrosion, and abrasion resistance; increased hardness	Variety of pure metals, carbides, nitrides, borides, silicides, and oxides of metals
	Electron Beam Evaporation	Any electrically conductive material stable at high temps	High	Solvent emissions	Increased hardness; wear and corrosion resistance; insulating, resistive, conductive, and decorative properties	Metals
	Ion Beam Assisted Deposition	Metals, plastics, glass	High	Solvent emissions, contaminated oils	Improved hardness, wear and corrosion resistance	Metals, metal alloys, dielectric and insulating materials
	Ion Implantation	Any solid	High	Solvent emissions, contaminated oils	Improved hardness, wear and corrosion resistance	Alloys of most elements (gases and metals)
	Ion Plating	Conductive and non-conductive substrates	High	Solvent emissions; metal exhaust vapors	Corrosion resistance	Metals, alloys
	Physical Vapor Deposition	Metals	High	Solvent emissions, solid waste	Oxidation, corrosion, and wear resistance	Metals, ceramics, semiconductors
	Sputtering	Metals, non-conductive materials, plastics	High	Solvent emissions; solid waste	Corrosion resistance; durability; resistance to impact; decorative, insulating, and reflective properties	Metals, metal alloys, dielectric and insulating materials
	Vacuum Metallizing	Metals, plastics, glasses, papers, and fabrics	Moderate	Solvent emissions	Reflective, absorptive and decorative properties; corrosion resistance	Metals

such as cadmium and hexavalent chromium that can be detected in the air or in wastewater found in metal finishing plants.

Traditional finishing processes such as electroplating often produce hazardous wastes that are increasingly expensive and difficult to dispose of because of the above mandates. Non-traditional metal finishing techniques such as ion implantation and IBAD are receiving increasing attention because of the rising environmental

remediation costs of the standard techniques. The following sections describe the ion implantation and IBAD techniques.

## 2.2 Ion Implantation

The technique of ion implantation was developed during the early 1960's as a method to introduce precise quantities of electrically active or dopant ions into semiconductor materials of micro-electronic devices. It is now the standard

semiconductor processing technique for providing these dopants.

Table 2-2 summarizes the history of ion implantation of metal substrates. Ion implantation of metal substrates began in the early 1970s. Following the work of Harwell Labs in England, the Naval Research Laboratory (NRL) initiated a MANTECH Program in ion implantation to determine if the process had potential for DoD aerospace bearings. Spire Corporation was the contractor for this effort. A large portion of the work performed by Spire was related to the development of hybrid implantation processes that they later enhanced for medical applications.

**Table 2-2. History of Ion Implantation Technology Development**

Year	Activity
1971	<ul style="list-style-type: none"><li>Implantation in semiconductors commercialized</li><li>Research started on implantation of metals at UK Harwell Labs</li></ul>
1976	First Harwell prototype implanter for metal substrates
1982	Navy MANTECH program on ion implantation started.
1983	First US commercial implanter for metals developed.
1985	Second Harwell prototype metal implanter
1986	Japanese AMMTRA project started
1990	Prototype PSII implanter developed (University of Wisconsin)
1992	MEVVA metal ion source commercialized.
1994	CCAD nitrogen implanter installed
1994	<ul style="list-style-type: none"><li>LANL/GM PSII CRADA</li><li>NDCEE/CTC environmentally safe alternative coatings effort started</li></ul>

During the NRL MANTECH Program, a private sector venture called Zymet Corporation was initiated by Eaton Corporation to try to take

advantage of the technological lessons learned during the MANTECH Program. The purpose was to design a cheap commercial implanter capable of implanting and refurbishing machine tools, dies, and punches initially, and other applications after the technology and concept were proven. The implanter that resulted was a small machine, 20 inches in diameter and 12 inches deep, that could only handle parts on a 8 inch platen. This size limitation restricted its applicability. The venture, though, also ran into a number of other obstacles.

First, Zymet had a difficult time convincing tool and die makers to try ion implantation. The Zymet President believes this may have been a "visibility quality control" problem. Since the tools and die makers couldn't measure or visibly see the effect of the implant, they had to be convinced that Zymet had actually done something with the part. Second, the tool and die market was a very conservative market. Most of the tool and die vendors saw no reason to change their way of doing business. Also, whenever a tool or die wore down it was typically replaced with a new tool or die and the old one was thrown away. There simply was not a large refurbishment market.

Before Zymet closed operations, they sold 15 implanters, most of which are still operational. Some were sold overseas, one was sold to Beamalloy Corporation in Dublin, Ohio, and two were purchased by Implant Sciences Corporation in Beverly, Massachusetts.

Besides Zymet, other companies also tried to market IBP technologies during the early-to-mid 1980s for metal surface applications. These companies included Ionic Atlanta, Ion Surface Technologies and Omni Implantation. When Zymet closed operations the entire industry appeared to lose its primary marketing focus. As a result, the three other companies mentioned above also soon went out of business.

The primary thrust in the attempts to commercialize ion implantation technologies has been to modify surface properties such as wear and corrosion by implanting appropriate alloying elements (see Table 2-3). Metal implants, in contrast to semiconductor implants, require high fluences to effect the desired property changes. Furthermore, the process has been in competition

with the other surface modification and coating techniques found in Table 2-1 such as electroplating, CVD, PVD, and thermal spraying. Most of the other techniques have thicker treatment depths and have been established in industrial practice. Consequently, penetration of the commercial market has not been as successful as ion implantation of semiconductors.

Research has demonstrated that properties such as hardness, wear resistance, coefficient of friction, fatigue strength, film adhesion, and corrosion resistance can be significantly improved by ion implantation. Table 2-3 summarizes the ion species that have been used to produce these improved properties.

**Table 2-3. Surface Properties Modified by Different Ion Species**

Surface Property	Substrate Material	Typical Implant Elements
Wear Resistance	Steels, ceramics, carbides, plastics	Ti, Ti&C, N, Y&N, Ti&Ni, Zr, Y, Y&C, O, C, B
Hardness	Metals, plastics, ceramics	Cr, Mo, Ti, Y, Zr, Nb, Ta
Friction	Ceramics, steels, plastics	Ti, Ti&Ni, Co, Cr, Ti&C
Fatigue Life	Metals	Ta, W, Re
Fracture Toughness	Ceramics, carbides	Zr, Cr, Ti
Corrosion Resistance	Metals, ceramics, glasses	Cr, Mo, Ta, Y, Ce
Oxidation Resistance	Titanium, superalloys	Y, Ce
Resistance to Hydrogen Embrittlement	Steels	Pt, Pd
Optical Properties	Glasses, plastics	Nb, Ti, Mo, Zr, Y

Even though ion implantation is relatively complex in terms of the equipment required, it is a relatively simple process. By removing electrons from atoms in a vacuum, a combination of positively charged ions and negatively charged electrons, called a plasma, is formed. Electric fields affect the plasma constituents. Positive electrodes attract the negatively charged electrons and repel the positively charged ions; negative electrodes attract the ions and repel the electrons. Ion implantation consists of basically two steps: (1) form a plasma of the desired material, and either (2) extract the positive ions from the plasma and accelerate them toward the target, or (3) find a means of making the surface to be implanted the negative electrode of a high voltage system. As seen in the sections that follow, case (2) applies to mass analyzed ion implantation and direct ion implantation, and case (3) applies to plasma source ion implantation. The system to form the plasma is called the ion source; the system to move the ions to the target is called the delivery system. The combination of the ion source and the delivery system is called the accelerator.

To better understand ion implantation, one can consider an analog with what happens when a concrete wall is shot with bullets from a machine gun. In this process the front surface of the wall is filled with bullets in the region close to the surface to a depth dependent on the mass and velocity of the bullets. In the same way the surface of a material struck by an ion beam will contain ions, be they gaseous or metal, from the ion beam. Unlike the bullet analogy, though, the implanted ions can combine chemically with the

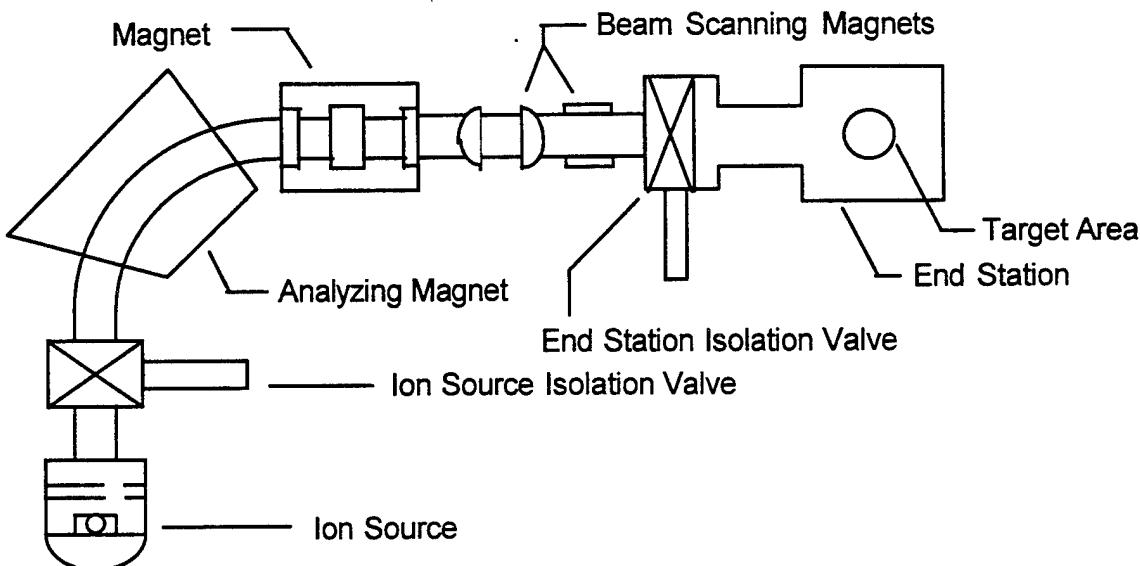
surface material. Additionally, whereas the wall is weakened by the bullet damage, the damage caused by ion implantation has actually been found to enhance properties by creating dislocations that suppress crack formation. This dislocation network has been found to contribute to increased hardness and wear resistance.

### **2.2.1 Ion Implantation Methods**

There are three methods commonly used for ion implantation. They differ in the way in which they either form the plasma or make the surface to be implanted the negative electrode. The three methods are mass analyzed ion implantation (MAII), direct ion implantation (DII), and plasma source ion implantation (PSII). All three methods are performed in a high vacuum chamber. They are isolated by the vacuum chamber from the outside environment. These three methods are further discussed in the sections that follow.

#### **2.2.1.1 Mass Analyzed Ion Implantation**

MAII is the technique that is used in semiconductor processing. It is also called mass-analyzed ion implantation. A typical MAII system is shown in Figure 2-1. In MAII, the plasma that is formed in the ion source is not pure; it contains materials that one does not wish to implant. Thus, these contaminants must be separated from the plasma. To perform this separation, the plasma source is placed at a high voltage and the part to be implanted is placed at ground. This produces a situation where the target is at a negative potential with respect to the



**Figure 2-1. Mass Analyzed Ion Implantation System Schematic**

plasma source. A negative electrode then extracts the ions from the source. The ions are then accelerated by a high voltage source to the target.

Between the ion source and the target is a large magnet, with magnetic field perpendicular to the direction of ion motion. Ions passing through this magnetic field are bent by the magnetic field. The amount of bending depends on the ion material being implanted and the strength of the magnet. Heavy ions bend less than light ions. By proper selection of the magnetic field, the desired ions can be steered to the target, while the undesirable ions can be expelled from the system.

The need for the magnets to separate the desired ions from the undesired ions makes mass analyzed ion implantation both very expensive - especially for applications where existing simple processes produce similar or better results as discussed in Table 2-1 - and limited in throughput. The magnet is costly to build and

consumes a very large amount of energy. In addition, the spread of the ions, or the ion beam, must be small in order to be properly bent to the target, but the number of ions cannot be very high because self-repulsion (remember that all of the ions have a positive charge) will cause the beam to diffuse. For the formation of metal ions, mass analyzed ion implantation can also present a toxicity problem. To obtain high currents of metal ions, a plasma source is usually used that forms the plasma by initiating an electric discharge in chlorine or other toxic gas.

The great advantage of MAII systems is that they can be used to generate an ion beam of every element in the periodic table. Moreover, the ion beams that are generated, because of the bending magnet, are extremely pure. MAII is used extensively in the electronics industry to dope semiconductors precisely because such purity is very important. For other ion implantation applications, though, such as metal finishing applications, mass analyzed systems are less

useful because of their high costs, limited throughput, and toxicity concerns.

### 2.2.1.2 Direct Ion Implantation

DII eliminates the need for the current limiting magnet found in MAII by using an ion source that produces a plasma and ion beam of just the desired material. A typical DII system is shown in Figure 2-2. In DII, the plasma is formed in the ion source and the ions extracted at high energies in a wide beam, passing through a valve directly into the end station, where they ion implant parts within the target area. In such a case, the beam current density can be high (10-50 mA), costs are greatly reduced, and relatively high throughput processing is possible. For uniform implantation of workpieces with curved or multiple surfaces, though, either the beam has to be rastered across the surface of the piece or the workpiece must be handled with a rotating or tilting platen or some other manipulator. As will be discussed below, the primary ion species used for direct ion implantation of metals are nitrogen gas and metal vapor.

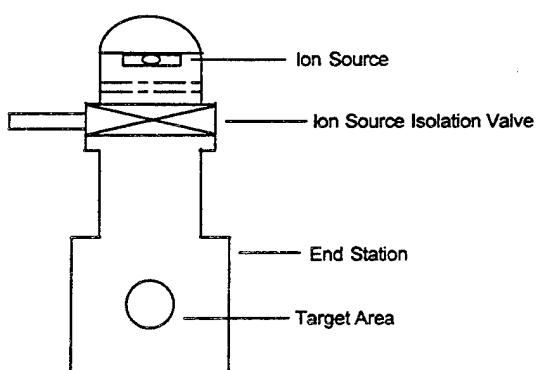


Figure 2-2. Direct Ion Implantation System Schematic

### 2.2.1.3 Plasma Source Ion Implantation

A final variation of the ion implantation process is the simplest in concept: make the material to be implanted the negative electrode. Figure 2-3 depicts a typical PSII system. In PSII (sometimes referred to as plasma ion immersion), the plasma source floods the chamber of the end station with plasma. Ions are extracted from the plasma and directed to the surface of the part being ion implanted by biasing the part to very high negative voltages using a pulsed, negative high voltage power supply. Because of the bias, the ions impinge virtually at nearly 90 degrees to all of the external surfaces, the optimum ion implantation angle.

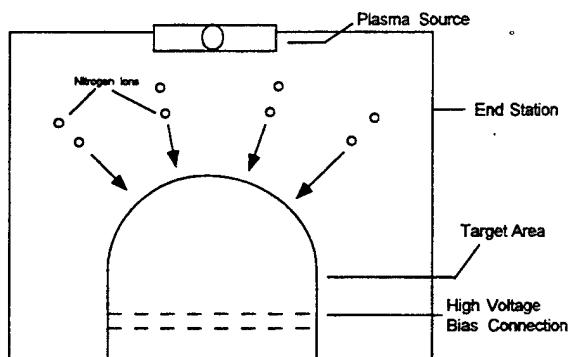


Figure 2-3. Plasma Source Ion Implantation System Schematic

While PSII is the simplest in concept, it is perhaps the most difficult in practice of the three ion implantation methods. To make this process work, the negative bias voltage imparted to the part to be implanted must be pulsed with a very short pulse length. Otherwise, an arc will form between the part to be implanted and the chamber walls or other grounded electrodes,

damaging or destroying the part. A second problem is regulating the amount of plasma that hits the surfaces of the part, and regulating where it goes. Ion beams are easy to measure and direct; plasmas are not.

PSII also lacks the versatility of MAII or DII. It cannot treat insulators without additional equipment, adding to the system complexity. It is virtually limited to gas ions.

There are safety problems that must be dealt with in PSII as well. Specifically, the parts being implanted using PSII will emit high energy electrons when they are hit by the high energy ions. In MAII and DII, the emitting electrons have very little energy and do not cause a problem. In PSII these electrons are provided a significant amount of energy from the negative bias voltage. They have enough energy to produce x-rays when they strike the chamber walls. Thus, PSII chamber walls must be shielded with lead.

### **2.2.2 Ion Implantation Species**

Nitrogen gas ions and selected metal ions are generally used for ion implantation of metals. The direct ion implantation method is the preferred method to implant both types of ion species. The characteristics of these two technologies are discussed in the sections that follow.

#### **2.2.2.1 Nitrogen Ion Implantation**

Nitrogen ion implantation for surface modification of metals was pioneered in the United Kingdom (UK) by Harwell Laboratory in

the early 1970's. Nitrogen was chosen because the value of nitrogen in steels is well known and because intense nitrogen beams are easily produced. The technology of high intensity nitrogen ion beams was perfected in the course of nuclear fusion programs. Since the development of the nitrogen ion implantation process by Harwell, numerous companies have tried to market the technique for surface modification of metals. As will be seen in later sections of this report, however, the technique has not been widely accepted despite numerous successful demonstrations.

In a typical direct nitrogen ion implanter, nitrogen gas is fed into the ion source, where electrons emitted from a hot filament ionize the nitrogen atoms and molecules, forming a plasma. Nitrogen ions are then extracted from the plasma, focused into a beam and accelerated through a voltage drop, typically about 100,000 volts. The accelerated beam of nitrogen ions is directed at the surface of the part to be implanted in the vacuum chamber. This is the same process described in Section 2.2.1.2.

Nitrogen ion implantation increases wear and fatigue resistance, lubricity, and in some cases, corrosion resistance of metal surfaces. In addition, nitrogen ion implantation has been found to increase the wear life of parts treated with hard chromium (hexavalent chromium) electroplate by between 5 and 10 times. Thus, nitrogen ion implantation has the added environmental benefit of reducing the need to perform the hard chromium electroplating

process by extending the life of the electroplated coating.

#### **2.2.2.2 Metal Ion Implantation**

Metal vapor ion implantation is a more recent development than nitrogen gas ion implantation. The technological development that led to the development of this process was the invention of the metal vapor vacuum arc (MEVVA) ion source at Lawrence Berkeley Laboratory. ISM Technologies in San Diego has perfected the ion source and provides both MEVVA-based ion implantation equipment and metal ion implantation services worldwide.

Similar to the source used in nitrogen ion implantation, the MEVVA source bombards a workpiece's surface with accelerated ions. In the case of the MEVVA source, though, metal vapor ions are used instead of nitrogen gas ions. Chromium, nickel, platinum and titanium are metal elements that have been implanted using this process.

One should again note that the normal pollution problems associated with these metals are alleviated because the entire implantation process takes place in a sealed vacuum chamber isolated from the outside environment. The plasma in a MEVVA ion source is generated by a cathodic or vacuum arc. The arc produces a very small (1 micron in diameter) cathode spot on the surface of an ion-forming metal that is co-located in the source, and acts to create a broad beam of ionized metal vapor that is directed toward the target workpiece.

### **2.3 Ion Beam Assisted Deposition**

The IBAD process combines ion implantation with physical vapor deposition (PVD), usually in the form of electron beam evaporation. The result is a coating that has been shown to improve corrosion resistance, lower the coefficient of friction, and improve wear life of pieces being coated. The work which demonstrated these properties of IBAD films was done chiefly by researchers in the field of thin optical films during the late 1970s and the early 1980s. Thus, IBAD developed independently of ion implantation. However, it was always understood by the implantation community that the shallow depth of penetration of ion implantation was a major limitation to the development of certain applications.

The advantages of ion implantation are high adhesion, bulk density, low substrate temperature, good reproducibility and control, and absence of catastrophic stress levels. The advantages of PVD are the formation of thick films, a wider range of film composition and low cost. IBAD combines the advantages of ion implantation and PVD. For this reason, many researchers in the ion implantation community such as Spire Corporation have also developed significant IBAD capabilities.

Figure 2-4 shows a typical IBAD system. A vapor flux of atoms is generated and deposited on a substrate using a PVD technique such as evaporation. Simultaneously, gaseous ions are extracted from a plasma similar to the manner described above for ion implantation and accelerated into the growing PVD film at relatively low energies (100 to 1,000 electron volts). The ions drive evaporated atoms into the piece part being coated and produce a graded interface between the part and the PVD coating,

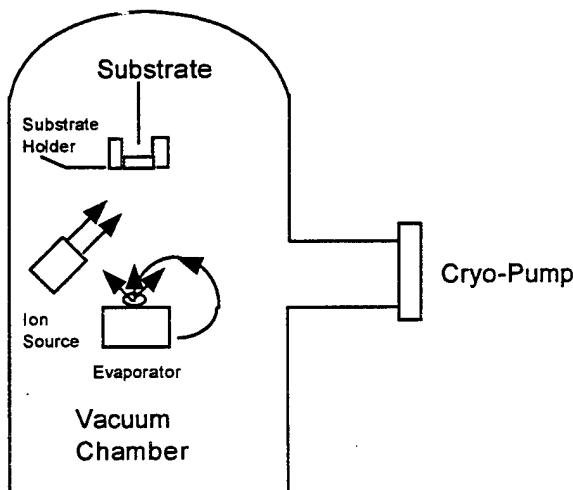


Figure 2-4. IBAD System Schematic

resulting in improved coating adhesion, film densification, residual stress modification and grain size/morphology modification.

In principle, there is no stipulation as to how the vapor or ion fluxes are generated. Electron beam evaporators are generally used to produce the vapor flux or evaporated atoms to be deposited. These evaporators are used because they are capable of evaporating a wide variety of materials with a wide range of physical properties. Other methods such as sputtering are available but they can only deposit a limited range of materials. Gaseous element ion sources are available for IBAD. Metallic ion sources are also available but they typically produce lower current density, and thus lower penetrating energy, and also require more complicated geometries.

### 3.0 IBP INDUSTRY DEMOGRAPHICS

This section provides an overview of the demographics of the IBP community. The capabilities and R&D interests and pursuits of companies involved with IBP technologies (both hardware and service providers), Government IBP players, and IBP technology researchers, as well as international players are described. Collaborative teaming arrangements, market areas, and current and potential applications are discussed.

### 3.1 IBP Companies

Companies involved in studying and advancing IBP technologies include those companies which provide and manufacture the equipment used in the process of IBP, and those actually involved in applying these technologies to various applications. Table 3-1 illustrates the key players in the IBP technologies area and their areas of concentration and study. Also, the table depicts if the companies are currently working in other metal surface finishing technologies such as electroplating, ion beam mixing, and semiconductor ion implantation.

Table 3-1. IBP Capabilities of Companies

Company	Hardware Provider	Service Provider	Researcher	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
Beamalloy		X	X	X			X	X <sup>2</sup>
Boeing			X			X	X	X <sup>1</sup>
Eaton Corp.	X		X			X		X <sup>3</sup>
Empire Hard Chrome		X	X			X		X <sup>1</sup>
Epion Corp.	X	X	X	X	X		X	X <sup>4</sup>
GM R&D Center		X	X			X		
Hughes Research Lab		X	X			X		X <sup>3</sup>
Implant Sciences	X	X	X	X	X		X	X <sup>2</sup>
ISM Technologies	X	X	X		X		X	X <sup>2</sup>
NDCEE								
Spire Corp.	X	X	X	X		X	X	X <sup>2,3</sup>
SwRI		X	X	X	X		X	X <sup>2</sup>

<sup>1</sup> Electroplating

<sup>2</sup> Ion beam mixing

<sup>3</sup> Semiconductor ion implantation

<sup>4</sup> Ion cluster beam

### **3.1.1 Beamalloy Corporation, Dublin, Ohio**

Beamalloy specializes in nitrogen ion implantation and IBAD coatings. Their business base is exclusively North American. Over the past decade, Beamalloy has developed ion implantation-based processes and systems used for volume processing of tools and wear applications to improve wear resistance, lubricity, or fracture resistance in ferrous and non-ferrous metals, ceramics, plastics, and glasses.

Beamalloy is also capable of performing extensive R&D. They pioneered the development of the process to nitrogen implant components that have already been chromium electroplated. This process promises to extend the life of chrome plate treatments by up to ten times and reduce the need to perform the plating operation. Furthermore, it reduces processing and environmental remediation costs associated with the handling and disposal of the hazardous wastes associated with the chromium plating operation.

Beamalloy had sales of approximately \$1M in 1995, all in the United States and Canada. Unlike the other IBP technology service centers (Implant Sciences Corporation, ISM Technologies, and Spire Corporation), they do none of their business overseas.

### **3.1.2 Boeing Corporation, Defense and Space Group, Seattle, Washington**

Boeing's Defense and Space Group works on the Comprehensive Chemical Reduction Program being conducted at Boeing. The program is five years old and receives substantial funding. The principal goal of the program is the reduction of solvent and other volatile organic compounds/chemicals (VOC) usage, but reduction in the use of heavy metals, such as cadmium and chromium, is also a concern.

The Boeing group said that OSHA is the most important regulatory driver for the reduction of cadmium and chromium. Boeing has made the reduction of cadmium and chromium a priority. Cadmium poses special problems when parts which are cadmium-coated must later be reworked. Boeing no longer uses chromium acid anodizing solutions and is working to reduce the usage of chromium primers. When Boeing changes or replaces a process, their subcontractors world-wide must also change their processes to be consistent.

The Boeing team has looked at several alternatives to chromium electroplating, including thermal spray, ion implantation, and diamond-like carbon coatings. The study team reported that ion implantation provided better protection to mating surfaces than diamond-like carbon in wear tests that they conducted.

Boeing has not aggressively pursued IBP technologies, however. Boeing is concerned that IBP technologies are not yet mature enough to be used in production. The study team stated that they were hesitant to use ion implantation, despite their own test results, because they are afraid that it yields such a thin layer that it might wear off of the part. They are also afraid that by using a thinner coating layer, the dimension of the parts would change and render parts in the current inventory useless because of the change in dimensions. Boeing has looked at PSII and is involved in a collaborative effort with Los Alamos National Laboratory (LANL) to investigate this technology. Boeing is also considering working with ISM Technologies on using IBAD technology.

### **3.1.3 Eaton Corporation, Semiconductor Equipment Division, Beverly, MA**

Eaton Corporation primarily manufactures and refurbishes custom ion implantation equipment for semiconductor applications. All of the implanters that they manufacture and refurbish are standard inline beam implanters. Eaton offers three different types of implanter machines - high energy, medium current, and high current. They have designed these machines to maximize the flexibility of the equipment to cover a broad range of doses and energies. For instance, their high energy and high current machines can also be used for medium current applications, and medium current machines can be used for some high energy applications.

Eaton was one of the first companies in the U.S. to recognize the potential of ion implantation into metals. Based upon results of numerous R&D activities both within the government and private industry, Eaton launched a separate company in the early 1980's called Zymet specifically to develop ion implantation equipment for metal finishing applications and to develop a market for the ion implanted parts.

Zymet manufactured two types of implanters: the Z100 and the Z200. The Z100 was strictly a nitrogen implanter that was developed to implant small parts machine tools and anatomical prostheses. It was designed to cost 1/10th as much as normal semiconductor implanters and had a relatively small reaction vacuum chamber, on the order of one foot by two feet. The Z200 was essentially the same as the Z100 but was capable of both thin film and nitrogen implantation. It could also incorporate an electron-beam evaporator.

However, Zymet, after building 14 or 15 machines, closed operations. A number of reasons are cited for this failure. First, due to the relative immaturity of the technology and a lack of knowledge of the potential market, Zymet built unique implanters for specific tool and die sets. This made the price of the machines and the ion implanted parts prohibitively expensive for all but the most high value applications such as the medical applications. Second, Zymet had a difficult time selling the new technology due to its relatively exotic or "strange" nature. Their potential customers all used established metal

finishing processes that they were familiar with and trusted, so they wondered why should they try something else, particularly when it was more expensive. When Zymet did actually receive some parts to be implanted, they found that they had to convince their customers they actually did something with the parts since ion implantation did not change the dimensions or the appearance of the parts.

Since Zymet went out of business, Eaton has been much more cautious in its activities related to ion implantation into metals. Eaton representatives mentioned that two or three years ago, Eaton re-investigated diversifying its product line with implanters capable of implanting into metals. They still found, however, that the cost was prohibitive and that there was no substantive market. They have continued to re-examine the issue and look for potential niche applications. Eaton has investigated plasma source ion implantation (PSII) for automotive valves and truck pistons. This work has been led by Eaton's R&D Center in Milwaukee, WI, in conjunction with the University of Wisconsin in Madison.

### **3.1.4 Empire Hard Chrome, Chicago, ILL**

Empire Hard Chrome, and its subsidiary National Hard Chrome in Toronto, Canada, is one of the largest hard chrome electroplating centers in

North America. They are capable of performing a wide range of plating techniques in-house, including:

- Standard chromium electroplating,
- Chromium electroplating with explosive diamond impregnation,
- Chromium electroplating with molybdisulphide impregnation,
- Chromium electroplating with final polymer seal, and,
- Chromium electroplating impregnated with boron-carbide.

In addition, Empire Hard Chrome has an extensive network of business relationships with vendors of other surface treatment technologies. These treatments include the deposition of diamond-like carbon films, explosive cladding, thermal spray, and high velocity oxygen fuel (HVOF) spray.

Of most importance to this study is Empire Hard Chrome's ongoing relationship with LANL regarding PSII. Los Alamos' scientists installed a PSII system at a new Empire Hard Chrome facility in Chicago in the fall of 1995. This is the first PSII system to go into commercial operation and will first be operated by Los Alamos' scientists. The objective is that as the technology matures and more applicabilities are identified, Empire Hard Chrome technicians will eventually

operate the facility. This technology transition is partially funded by the Department of Energy (DOE).

### **3.1.5 Epion Corporation, Bedford, MA**

Epion Corporation has been a developer of ion beam process technology since being founded in 1984. The company is presently performing SBIR and other programs related to ion-assisted thin film growth, reactive ion synthesis of surface coatings and ion beam modification of surface properties. Epion also serves as a subcontractor to other companies under SBIR programs involving development of surface coatings and specialized ion implantation techniques.

Epion offers ion implantation services with capabilities for processing at temperatures up to 2400 °F (1300 °C), which are important for reactive synthesis. Epion employs its high temperature implantation facility to produce integral silicon carbide surfaces on diamond in order to provide protection of the diamond against high temperature oxidation. Implantations can also be performed together with concurrent in-situ processes such as deposition. Epion produces electrically conductive, chemically inert diamondlike coatings by ion implantation with concurrent deposition of carbon-containing materials from sublimation sources. Epion also has thin film deposition facilities employing excimer laser ablation in conjunction with in-situ ion bombardment.

Epion is developing equipment for processing by beams of gas cluster ions. Cluster ions, which are produced by passing a pressurized gas through an expansion nozzle into vacuum, are expected to have applications for ultra-shallow ion implantation, for sputtering, and for reactive synthesis. Epion will deliver a first cluster ion processing system to a customer in Japan in fall 1996 and will then offer similar equipment as a commercial product.

### **3.1.6 General Motors R&D Center Warren, MI**

The General Motors Research Corporation was the first automotive research organization in the automotive industry. Its mission is to develop new technology for GM and its products, and to pace the global industry with industry-leading innovation. GM is working in conjunction with LANL and the University of Wisconsin under a four-year cooperative R&D program to further develop PSII. The program's emphasis is on large-scale demonstrations aimed at increasing surface hardness for engine components.

### **3.1.7 Hughes Research Laboratory (HRL), Malibu, CA**

Hughes Research Laboratories is a subsidiary of General Motors and is part of Hughes Electronics. Hughes has combined their expertise in materials processing for heat treatments, and hard coating and surface modifications in an attempt to advance existing and new commercial markets. Hughes is

researching wet alternatives to cadmium and chromium electroplating in response to the demand for replacement of those materials. Some examples of alternatives are electroless nickel, with or without inclusions; Ivdized aluminum (IVD-Al) deposition; nickel-tungsten-boron (Ni-W-B); and iron-tungsten (Fe-W).

Hughes has worked in the area of plasma based surface engineering technologies since 1988 and many of these technologies stem from work done at Hughes in the last 30 years. Areas of research include heat treatment, hard coatings, and surface modification. Hughes had the PSII implanter with the largest chamber in the country from 1988 until LANL built a larger one in 1992. The chamber dimensions are approximately 8 feet long by 4 feet in diameter (2.4 meters by 1.2 meters).. The implanter requires a high-power (100 kW), high voltage (100-kV) pulse modulator to provide voltage pulses necessary for the implantation process.

Hughes was the first to develop a 100 kV, 100 kW processing capability in 1990, and was the first to demonstrate a 200-250 kV processing capability in 1995. They developed ultra-high-current PSII and thermally-enhanced PSII. Hughes uses low-pressure, partially ionized, high-density plasmas that are engineered for large-scale, conformal and uniform treatment of part. Their main objective in PSII research is to improve the tribological properties of metal and nonmetal (polymer) materials used in aerospace, defense and commercial applications.

HRL representatives indicated that their process allows for high-power continuous or pulse-modulated delivery of ions, electrons and metal atoms omnidirectionally and simultaneously onto the surface of parts in a faster and more efficient manner than is possible with conventional technologies. They have used this process to demonstrate the implantation of non-conductors and successfully reduced X-ray emissions from the process using electrostatic confinement to prevent electrons from interacting with a grounded plasma. Hughes demonstrated a 2-3X improved wear life for drill bits using PSII, 2 times improved hardness of polymers, 5 to 8 times improved wear life for titanium nitride (TiN)-coated cutting tools, 2 times improved wear life of TiN-coated sand abrasion parts, and enhanced the growth of wheat seeds subjected to implantation.

Hughes is involved in a project with GM Canada in London, Ontario to implant polymers with ions. Polymer implantation can increase the longevity of polymer dies and reduce energy consumption in manufacturing new dies. Hughes can handle large parts in its polymer implanter. A relatively low dose of ions is used in the process and it is very fast. Dose can not be directly measured in polymers, only the effects of the dose can be measured. The Hughes representative stated that currently there is no market for implanted polymers and the parts to be treated are too large to be economical.

Hughes has used nitrogen implantation to improve the surface properties of TiN. Implant

Sciences determined that implanting TiN with N improves wear resistance. TiN can also be enhanced with PSII. Hughes calls this process plasma material deposition (PMD) and has demonstrated an increase in cutting tool lifetime of a factor of 18 compared to a factor of 5 for the best conventional TiN coating processes.

Titanium carbonitride provides higher surface hardness than Ti-N. However, titanium carbonitrate emits cyanide when coated with conventional processes. Thus, there are additional environmental costs associated with the conventional processes as a result of the cyanide emissions. If methane is implanted into TiN using PSII, titanium carbonitride can be formed without cyanide emissions.

Hughes has developed a nitrogen implanted TiN coating that is purple after the implanted region is worn away. This is useful because when a part is worn, the color of the surface changes. This is particularly useful in die applications where it is difficult to determine when the die is worn and needs to be replaced. The conventional testing method involves measuring the dimensions of the die with a very accurate stylus. This is expensive and requires the die to be taken out of service and into a lab for measurement. Another method is to simply replace the die after a specified time or number of manufactured parts. This can result in discarding expensive dies which still have a useful production life. The Hughes color change method is easy to use and could be very cost effective. GM and Hughes both have patents on this process.

Hughes pursued Advanced Research Projects Agency (ARPA) funding for large-scale Intelligent Plasma Processing of Materials (IPPM). This was to be part of a regionally advanced manufacturing program (RAMP). A RAMP focuses on small vendors who cannot afford to invest in new technologies on their own. Hughes hoped to get RAMP funding for a three year project to investigate chromium electroplating replacement technologies, but didn't receive funding for the project.

Hughes representatives see plasma-based processing of materials as an open opportunity for motor vehicle components and manufacturing applications. Hughes has assembled a vertically integrated team including GM, academic institutions, research labs, and other end users to work on the project. The program is currently funded half by GM and half by Hughes.

### **3.1.8 Implant Sciences Corporation, Wakefield, MA**

Implant Sciences is a ten-year old IBP technology service provider that also manufactures and refurbishes both mass-analyzed and direct ion implantation equipment. ISC has research, service and equipment capabilities in ion implantation, ion beam-assisted deposition, tribology, and related software. Ion implantation services available include over 60 ion species, rare earth and noble metals, and implantation from cryogenic temperature to well over 1000 degrees Celsius (°C). ISC manufactures systems for ion implantation, IBAD, and measurement of

wear and friction and coating adhesion. They implant approximately 50,000 piece parts per year, the majority of them being medical components - about 25,000 knee and hip balls. They are presently working two shifts.

Onsite in Wakefield, MA, Implant Sciences has eight machines, two of which are Zymet machines that Implant Sciences purchased when Zymet went out of business. They also have the facilities that comprised the Navy MANTECH ion implantation project, which focused on the potential of this technology for DoD aerospace bearings that was managed by NRL in the early 1980's.

Implant Sciences recently won the contract to provide the National Defense Center for Environmental Excellence (NDCEE) with a 12 feet long by 6 feet in diameter (3.6 meters by 1.8 meters) vacuum chamber. When completed and installed, this chamber will be the largest known implanter and IBAD system in operation in North America for metals. This will allow the implantation of larger work pieces and also increase throughput for smaller parts.

### **3.1.9 ISM Technologies, San Diego, CA**

ISM Technologies is primarily an IBP equipment manufacturer, but also advises clients on how to take IBP processes into production and does some basic research on IBP technologies. The company was founded in 1986 to commercialize the Metal Vapor Vacuum Arc (MEVVA) ion source, developed at Lawrence Berkeley

Laboratory (LBL), with the focus on using the MEVVA for metal ion implantation

ISM has been manufacturing MEVVA metal ion implantation systems for sale world-wide. ISM markets the metal ion implantation of cutting tools using MEVVA technology such as ToolPeen. The ToolPeen process involves implanting cutting tools with titanium (Ti) and nickel (Ni) ions. ISM has demonstrated increases in wear life for cutting tools of up to a factor of 4.8 after treatment with ToolPeen. The cost of ToolPeen varies from \$0.05 to \$0.50 per square centimeter depending on the implantation equipment's capacity and throughput. Cost is low enough to use the process on automobile engine valve stems, piston rings, cam followers, and similar parts. The MEVVA 480-10, a 10 milliamp metal ion machine, has an installed cost of \$450,000. Many of MEVVA 480-10 machines are being used for research and development in Japan and China.

ISM uses MEVVA technology in other applications as well. It can be used on metals, ceramics, glasses, and plastics. Because it is a non-thermal process, materials with low melting temperatures can be treated. Other applications include reducing friction in ceramic engine parts; reducing stress crack corrosion, wear, and friction in bearings; reducing scuffing wear in gears; and reducing hydrogen embrittlement in airframe parts. ISM expects the ToolPeen business to increase this year by 50 percent and plans to purchase more implanters. The

company expects that ToolPeen sales will continue to grow through 1997.

ISM has built the largest commercial metal ion implanter in North America called the MIP 4-500. The approximate chamber dimensions are 6.5 feet long by 5 feet in diameter (2 meters long by 1.5 meters in diameter). It is six times larger than any other metal ion implantation system in the market. Up to four Advanced Vacuum-arc Ion Sources (AVIS) can be operated by the single 80 kV, 500 mA, power supply. ISM has developed proprietary software to operate the implanter, which runs under the Windows operating system. The AVIS source consists of an array of motor-driven cathodes with a wide area extractor design. The AVIS source can create a beam with a rectangular area approximately 3.2 feet by 1.6 feet (1 meter by 0.5 meters). AVIS produces a pure beam of most metals, including platinum (Pt), of up to 500 mA at 80 keV. Two elements can be easily implanted on complex surfaces using this source. AVIS can be used in conjunction with the multiple ion source production implantation system (MIP), which is a production scale system. Up to four ion sources can be controlled by a single power supply and beams can be brought in at different angles. The beams can be as large as 3.2 feet by 3.2 feet (1 meter by 1 meter).

ISM has developed the Hyper Ion (H-I) process for the non-reactive deposition of coatings such as titanium diboride ( $TiB_2$ ) and TiN. In the ISM H-I process, high-energy ions are produced from

a cathodic arc ion source and short, very high-voltage pulses are applied to the substrate during the deposition process. ISM has investigated the use of the H-I process as a chromium electroplating alternative for the U.S. Air Force. The process yields good dense coatings at temperatures as low as 150 °C for TiN. Aluminum and certain alloyed steels can be coated with this process without degrading their mechanical properties because of the low heat.

The H-I process has applications in DoD where it can be used on titanium since high temperature coatings cause oxidation of titanium. An example application where this occurs is in turbine blades in aircraft engines. H-I can also be used for cleaning surfaces prior to treatment, especially for the removal of oxides.

In addition, ISM is working with Eaton Corp. on using the H-I process to treat automotive valve stems, and with Corning Corporation to replace chromium plating on molds for television tubes.

ISM developed the inner bore ion source (IBIS) for National Aeronautics and Space Administration (NASA). IBIS is a filter technique for cathodic arc and is used by NASA to coat samples with gold. IBIS can also coat the inside of surfaces and ISM will use this capability in a contract with the U.S. Air Force.

ISM main business base is in the Japanese market. The Japanese industries have acquired millions of dollars of ISM equipment, and have committed to purchasing millions of dollars of

more equipment. Per ISM representatives, Nippon Steel Corp. currently uses the MEVVA ion implantation equipment for automobile components. Kobe Steel, Ltd., the largest manufacturer of PVD coating systems and the largest tool manufacturer in Japan, uses ISM's MIP system for the implantation of shop tools such as cutting and molding tools.

ISM has done a lot of work on the implantation of polymers with excellent results. They have observed a depth effect similar to that observed with metals. Hardness and elasticity have been increased significantly. ISM believes that implanted polymers could replace metal parts in automotive and aerospace applications. Some of the polymer implantation work was done in conjunction with Oak Ridge National Laboratory (ORNL).

### **3.1.10 National Defense Center for Environmental Excellence (NDCEE), Johnstown, PA**

NDCEE was established by the DoD in 1991 to lead and support DoD facilities and the associated industrial base in adopting a comprehensive approach to pollution prevention, and to address other high priority environmental issues. Its mission is to transition environmentally acceptable technologies to defense activities and private industry, to provide training in the use of new technologies, and to support applied research and development to transition new technologies. NDCEE is operated by Concurrent Technologies Corporation (CTC), an independent nonprofit corporation, and is

interfaced to DOD through the Army's Environmental Technology Office (ETO) at Picatinney Arsenal, NJ.

The DOD, through the ETO, has contracted with NDCEE/CTC for an ion beam processing project on an ion beam processing effort to investigate the applicability of ion beam processing as an alternative to less environmentally-friendly electroplating operations. They are in the process of identifying replacement applications for ion beam processing and selecting materials/components for demonstration. One of the primary purposes of this effort is to develop a model of how the ion beam techniques can be inserted into the defense and commercial industrial base. The effort is geared towards identifying niche opportunities that the ion based techniques can fill within DoD, and also highlighting the technologies. This has been a problem in the past because the surface finishing market is so diverse and there are always competing technologies for any type of surface finishing requirement. This is in stark contrast to the semiconductor industry where there are no other techniques to provide dopants in a highly controlled manner.

Once CTC has the large new nitrogen implanter built by Implant Sciences installed, they will also act in a "service center" role by allowing companies with surface finishing requirements to bring in their components for low risk trials of IBP technologies. This pilot scale ion beam processing system will allow NDCEE/CTC to compile cost/benefit data and define a material

specification for an ion beam process. CTC has also been able to test the performance of the coatings or implants using standard techniques such as scratch tests or salt spray tests. Once an opportunity is identified and tested, CTC will work with original equipment manufacturers (OEMs) to further implement the process.

Other organizations sponsoring this program at NDCEE/CTC are the U.S. Army Production Base Modernization Activity (PBMA), NJ, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, U.S. Naval Research Laboratory, Washington, D.C., Corpus Christi Army Depot (CCAD), TX, Jacksonville Naval Aviation Depot, FL, Basic Industrial Research Laboratory (BIRL)/Northwestern University, Evanston, IL, Los Alamos National Laboratory, NM, and U.S. Army Aviation and Troop Command (ATCOM), St. Louis, MO.

### **3.1.11 Southwest Research Institute (SwRI), San Antonio, TX**

SwRI is an independent, nonprofit, applied engineering and physical sciences research and development organization with 13 technical divisions. SwRI has invested in an ion implantation facility in which the surfaces of all kinds of materials can be modified using energetic ion beams. Their plan is to develop advanced processes to overcome surface-related problems for client organizations in a variety of tools and component. To date, they have demonstrated dramatic reductions in the wear in orthopedic materials and lower friction in

ceramics. They are in the process of formulating ideas that could lead to novel electronic device structures.

SwRI is currently focusing research on the following selected applications. Under an Institute internal research project, and in participation with the University of Texas Health Science Center at San Antonio, they are conducting research into the orthopedic application of diamond-like carbon (DLC) to combat wear of polyethylene components in replacement hip and knee joints. Their results demonstrate that a DLC coating applied to a widely-used cobalt-chrome alloy implant reduces wear of polyethylene under conditions similar to those in the body to a level where it is no longer measurable. The improvement is between one and two orders of magnitude, which could considerably extend the wear life of a hip joint. This research could be applied to a variety of biomedical materials, including heart valves, neurological electrodes, and catheters.

Another application area they are pursuing is in reducing dependence on chromate baths for the surface treatment of aluminum alloys through an ion assisted process. The researchers believe that this process could overcome the pollution and industrial discharge problems associated with toxic hexavalent chromium. A third thrust is in the use of nitrogen ion implantation to extend the lives of tools used in injection molding and extrusion of filled polymers. And finally, they are conducting R&D into the electrical properties

of DLC to assess its commercial potential for use in fabricating simple electronic devices.

SwRI believes that successful demonstrations and field trials of ion beam-modified materials will lead to the need for large-scale, dedicated equipment to be operated in-house by their client organizations. They are poised to provide designs for such equipment, or to team with a manufacturer to supply it to the client's specifications.

The IBP technologies to be used and further developed at the facility allow the coating of items with a surface area of several square feet. It also allows low processing temperature, and therefore can be applied even to polymers. In the early stages of its development, the vacuum chamber in SwRI's ion beam facility will be equipped for ion beam-assisted deposition and diamond-like carbon coating. In subsequent stages, additional ion guns will be installed on the spare ports and flanges provided. Their function will be to enable ion implantation with gaseous and metallic species to improve resistance to wear and corrosion. When fully operational, ion beam processes that can be carried out at this facility include ion implantation of metallic and gaseous ions, IBAD, ion beam mixing, and implantation of various forms of DLC.

The ion beam processes will be conducted in a stainless steel vacuum chamber six feet long and four feet in diameter - purported to be the largest such device in the U.S. dedicated to ion beam

surface modification. This will allow trials to be made on large, full-size tools and components.

Future plans include installation of a robotic manipulator inside the vacuum chamber, so specimens can be exposed controllably to sequential treatments using a variety of ion beams or coating fluxes.

### **3.1.12 Spire Corporation, Bedford, MA**

Spire Corporation is a manufacturer of IBP equipment and a researcher in the IBP technology area. They also provide equipment for medical applications. Spire manufactures and refurbishes inline beam ion implantation equipment and provides custom ion implantation services for both semiconductors and metals. Spire is considered one of the preeminent ion implantation research, development, and production firms. They have invented many of the processes that are used world-wide today, such as the titanium implantation technique used to implant medical prostheses.

The largest market presently for Spire is the medical market. The company has provided numerous ion implanted metal components for over a thousand medical applications such as hip joints, knee joints and catheters since entering into the medical market in 1985. Spire coordinates directly with the original equipment manufacturers (OEMs) who supply the finished part to the medical community. The surface engineering technology area, of which ion implantation is a part, comprises 35% of Spire's

overall business base. Ion implantation of medical components is approximately 95% of Spire's ion implantation business. They are presently working three shifts per day, seven days a week to fill all of their medical component orders.

Spire was able to develop much of their expertise in ion implantation production processes SBIR programs with the DoD and grants from other agencies such as the National Science Foundation (NSF). The development of the medical application area, though, had to be thoroughly coordinated with the Food and Drug Administration (FDA), National Institutes of Health (NIH), and medical device OEMs.

Spire representatives indicated that gaining acceptance of ion implanted components was a monumental undertaking; one that would not have been possible without the support of the OEMs. They also pointed out, however, that the medical industry is unique in that it is willing to pay a premium for high quality products since most of the components are being surgically inserted into the human body. In this respect, the medical industry is much like the semiconductor industry. Both doctors and patients demand components that perform at or near 100 percent efficiency. In addition, Spire indicated that the cost of implanting a component such as a hip joint is approximately 10 percent of the total cost of the part.

A large portion of Spire's medical component business is implanting nitrogen and carbon into

replacement titanium hip balls. Spire experimented with many combinations and ratios of implanted species until they found a recipe that reduces scouring and friction in the hip joint. Another large percentage of their implantation business is the implantation of a cobalt-chromium-molybdenum compound into a high molecular weight polyethylene used for low friction surgical tubing. All of the implants for the medical applications are done using mass analyzed, inline beam ion implantation in order to meet the highest quality standards.

In addition, researchers at Spire are working on a method of nitrogen ion implantation that strengthens the surface of titanium alloys, helping the materials resist fretting. This research is being funded by the U.S. Air Force. The treated parts doesn't propagate vibrations across their entire length, so they resist the jostling that induces early part fatigue. These parts also have a lower coefficient of friction, increased microhardness, and a lower rate of chemical corrosion. They are planning to install these parts in aircraft engines and simulate their performance against that of standard blades with a conventional antigalling coating. The U.S. government is funding this effort. After completion of this effort, Spire will seek out makers of aerospace disks and blades to further develop this technology, which will be licensable.

Spire has also investigated many other markets and applications for ion implantation. One such market is the automotive industry. In their

opinion the automotive industry is not yet prepared to embrace the technology because the automakers are very cost conscious. If a part costs \$1 or 1 cent more when ion implanted as opposed to electroplated, the part will not be used because they are not willing to absorb or pass on that extra cost in the highly competitive automotive marketplace. Spire has been working with GM R&D Center and GM's Cadillac Division to find the proper niche for ion implanted automotive parts.

In addition to mass analyzed ion implantation, Spire representatives stated that Spire was one of the first companies to research plasma source ion implantation (PSII). They indicated that PSII does reduce the cost of implanted parts, but the process compromises the quality of the implant. Inline beam ion implantation is still more reliable, more reproducible, and produces higher yield.

Spire is also investigating ion beam assisted deposition (IBAD) techniques. They have invested millions in a teaming arrangement with an Italian multinational firm to develop an IBAD technique for the replacement of cadmium electroplating of sheet steel. Spire believes that large scale production is possible with this process. This effort is a two to three year project and has just gotten underway.

### **3.2 Government IBP Technology Researchers**

In this section, the capabilities and initiatives of Government IBP technology researchers are

highlighted. It describes their current R&D efforts and interests, cooperative teaming arrangements, areas of funding, and targeted potential applications of the technology. Table 3-2 provides a snapshot view of these players and their IBP technology areas of research.

#### **3.2.1 U.S. Department of Defense (DoD)**

DoD has been interested in IBP technologies as a potential replacement for cadmium and chromium electroplating, as well as the possible enhancement of surface properties. Table 3-3 highlights the current U.S. Army IBP R&D projects that have been undertaken. Table 3-4 highlights U.S. Navy initiatives in this area. The project descriptions depict accomplishments to date. Then, the current status, projects and efforts of DoD technology researchers are presented.

##### **3.2.1.1 U.S. Army Research Laboratory (ARL), Aberdeen, MD**

ARL's Material's Laboratory (formally the Army Materials Lab in Watertown, MA) directs the Basic Research and Exploratory Development research in IBP technology shown in Table 3-3 within the U.S. Army. They are co-technical monitors of the ongoing work at NDCEE/CTC related to environmentally acceptable alternative coatings for cadmium and chromium electroplating. ARL researchers are the U.S. Army's most prominent proponents of IBP technologies for metal surface finishing applications.

Table 3-2. Capabilities of the Government IBP Technology Researchers

Agency	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
DoD					
ARL	X			X	X <sup>2,3</sup>
ARPA					X <sup>4</sup>
CCAD	X				X <sup>1</sup>
NRL	X			X	X <sup>2,3</sup>
Wright Lab				X	
DOE					
LBL		X			
LLNL	X				
LANL			X		
ORNL	X			X	
Other					
EPA					X <sup>4</sup>

<sup>1</sup> Electroplating

<sup>2</sup> Ion beam mixing

<sup>3</sup> Semiconductor ion implantation

<sup>4</sup> Proponent

**Table 3-3. U.S. Army IBP R&D Projects**

PE	PE Title	Proj.	Project Title	Year	Project Description
0601102A	Defense Research Sciences	AH42	Materials and Mechanics	FY94	Demonstrated ion beam technique to improve wear and corrosion resistance of rotary winged aircraft components.
				FY95	Optimize dry ion beam treatments as environmentally acceptable alternatives to cadmium/chromium electroplating, and optimize surface treatments to reduce hydrogen embrittlement of high strength armor steel.
0601104A	Univ./Industry Research Centers	BH64	Materials Center of Excellence	FY96	Conduct research in corrosion effects and protection of alloys
				FY97	Conduct research in corrosion effects and protection of alloys
0602105A	Materials Technology	AH84	Materials	FY94	Demonstrated improved wear corrosion resistance in aircraft materials using ion beam processes and corrosion resistant schemes for advanced magnesium aircraft components.
				FY95	Optimize dry ion beam treatments as environmentally acceptable alternatives to specific cadmium/chromium electroplating applications; develop multi-functional protective coatings.
0602720A	Environmental Quality Technology	D048	Industrial Operations Pollution Control Technology	FY96	Develop preliminary guidance on air toxics from plating operations
		A829	National Defense Center for Environmental Excellence (NDCEE) Technology	FY95	Provide technology transfer and transition of DOD efforts, including electrodeposited coatings

Source: U.S. Army 1996 Congressional Descriptive

Summaries

**Table 3-4. U.S. Navy IBP R&D Projects**

PE	PE Title	Proj.	Project Title	Year	Project Description
0708011N	Manufacturing Technology			FY94	Coatings and surface treatments will be developed to achieve wear, corrosion and thermal resistance for mechanical systems such as machine elements, tools, engine components, thermal systems and control surfaces. Research and technology development in manufacturing of diamond and related coatings and ion implantation systems.
				FY95	National Center of Excellence for Metalworking Technology: Continue work in Advance Surface Treatment and Component Wear; develop solutions to specific wear problems such as aircraft hookpoints through surface treatment technology developments.

Source: U.S. Navy 1996 Congressional Descriptive Summaries

**3.2.1.2 Advanced Research Projects Agency, (ARPA), Arlington, VA**

In 1994, ARPA commissioned a team headed by the Basic Industrial Research Laboratory (BIRL)/Northwestern University to demonstrate advanced technologies to eliminate hexavalent chrome and toxic wastes generated by hard chrome electroplating, and to reduce by 80 percent the solid waste volumes from chrome stripping operations. Among the solutions the team is researching are clean alternative technologies such as plasma nitride/PVD coatings. The project team consists of BIRL, Corpus Christi Army Depot (CCAD), General Electric (GE) Aircraft Engines, and the Naval Research Laboratory (NRL).

**3.2.1.3 Corpus Christi Army Depot (CCAD), Corpus Christi, TX**

CCAD is an U.S. Army helicopter rework facility. A major part of the helicopter rework process involves the use of taps and cutting tools to produce precision helicopter replacement components. The impact of ion implantation on tap and cutting tool performance was evaluated at CCAD as part of a cooperative program with ARL. The effort demonstrated that ion implantation improves the machine tool life of tools from 1.5 times to over 5 times. The CCAD/ARL ion implantation investigation, which began in 1985, resulted in the procurement of a large-scale production, direct nitrogen ion implanter by CCAD in September 1994.

### **3.2.1.4 U.S. Naval Research Laboratory, Washington, D.C.**

Ion implantation research at the Naval Research Laboratory (NRL) began in the early 1970s with some exploratory implants of semiconductor materials by NRL's Radiation Sciences Division. This work expanded in the mid-1970s into a cooperative program with NRL's Metallurgy Division by using heavy ion bombardment to study radiation damage in reactor materials. In 1979, an interdisciplinary research program was established to understand the physics of ion implantation to demonstrate the feasibility of specific applications, to identify areas of potential naval applicability, and to assist in the transfer of this technology to naval systems. In 1980, a medium current ion implanter was purchased and several in-house designed end stations were constructed for performing the studies. A considerable amount of fundamental research was performed in areas related to depth distributions of implanted ions, sputtering effects, surface chemical reactions, radiation enhanced diffusion, and phase transformations.

Ion implantation was viewed as being able to improve performance in a wide range of applications where the performance is controlled by surface composition or structure. Corrosion and wear reduction were among the first applications tested because they are the leading causes of loss of reliability and equipment failure. In the area of corrosion, NRL research identified at least three mechanisms by which ion implantation reduces the corrosion rate. Implanting palladium into titanium stimulates

the cathodic reaction and shifts the metal surface into an electrochemical passive state. Implanting phosphorus and boron into stainless steel created an amorphous surface layer that removes corrosion sites such as grain boundaries. The mechanism with broadest applicability was determined to be the implantation of elements known to form passive films that reduce the dissolution rate of the alloy. The best example is the addition of chromium to steel to concentrations exceeding 12 percent, producing "stainless" steel. Numerous studies were performed at NRL which showed that implantation of elements such as chromium and tantalum into low-alloy bearing steels greatly increased the resistance to either general or pitting corrosion in chloride-containing solutions. Pursuant to the laboratory studies, several turbine engine bearings from F-4 fighters and H46 helicopters were implanted with chromium and installed in operating aircraft. However, because no formal procedure for tracking these bearings was implemented, actual performance was never documented.

Related to wear, NRL research determined that titanium implantation into 52100 bearing steel produced a surface that showed no wear scar when subjected to an unlubricated sliding ball under a 2.2 pound (1-kg) load for 20 cycles, whereas an unimplanted sample showed scarring after only one cycle. In addition, the implantation reduced the friction coefficient by half. Other studies demonstrated significantly increased resistance to scuffing wear of titanium or tantalum-implanted hard steels such as M2 or 9310.

The favorable laboratory studies led to the Navy funding a Manufacturing Technology (MANTECH) project in 1982 to develop a prototype ion implantation facility that would be capable of processing components such as bearings on a semi-production basis. The objectives of this program were twofold: 1) to demonstrate improved performance by implanting actual components and installing them in operating Navy systems and 2) to document cost savings through a cost-benefit analysis that would include the cost of ion implantation balanced against the reduced acquisition costs of the components resulting from increased lifetime. The facility, which included a high-current Eaton semiconductor ion implanter (without the wafer processing end station) and a contractor-designed 120 cubic foot (1-cubic-meter) end station with component handling fixtures, was placed into operation at Spire Corporation in 1985. Numerous aircraft bearings were implanted, installed, and flight-tested. The cost of the processing was also documented. However, neither NRL nor Spire were able to attain flight qualification approval for the implanted bearings. This MANTECH project ended in 1986.

In 1989, the U.S. Army Acquisition Pollution Prevention Support Office (AAPPPO), Headquarters, U.S. Army Materiel Command (AMC) approached NRL about collaborating on a project to demonstrate ion implantation as an environmentally acceptable surface treatment technology. Pursuant to these discussions, it was decided that the U.S. Navy MANTECH ion

implanter would be used to implant test coupons for laboratory corrosion studies at ARL and then to implant bearings and other components from U.S. Army helicopters. Rig tests were performed on some implanted transmission bearings at CCAD, which showed no degradation in fatigue life. Although officials at the U.S. Army ATCOM indicated that they would be willing to issue an airworthiness certificate for the implanted bearings, final approval to install the implanted components on operational aircraft was not able to be obtained. If the recommendations of this report are implemented this issue will have to be revisited and addressed.

In 1994, the MANTECH high-current ion implanter was transferred to Implant Sciences Corporation (ISC), and a Cooperative Research and Development Agreement (CRADA) was established between NRL and ISC. ISC has attached their own large end-station to the implanter and the facility has been used to conduct research into a process called reactive ion implantation. In this process, ion beams are used to enhance surface chemical reactions to produce protective oxide films, for instance. The NRL/ISC implanter is also capable of processing components such as bearings, gears, shafts on a semi-production basis. The medium-current ion implanter is still operational at NRL and is available for coupon and small component processing. Both ion implantation systems can produce beams for virtually any element in the periodic table, with total beam currents ranging from a few hundred microamperes to ten milliamperes, depending on the element.

Currently, NRL is working with the Naval Air Warfare Center in Warminster, PA to investigate the use of ion implantation to reduce corrosion and wear on transmission gears on selected Naval aircraft.

### **3.2.1.5 Wright Laboratory, Wright-Patterson Air Force Base, OH**

The Plasma Research Group of the Aero Propulsion and Power Directorate at Wright Laboratories has recently installed a large area ultra high vacuum apparatus for ion beam processing. The equipment is used to produce high quality, large area thin films and to understand the fundamental science of ion beam deposition.

Experiments carried out to date at the facility have successfully deposited diamond-like carbon (DLC) and nitrogen doped DLC IBAD films on a variety of substrates. These substrates include silicon, quartz, aluminum, tantalum, molybdenum, stainless steel, polycarbonates, silicon carbide, nickel and copper. The effects of gas composition, accelerating power, substrate temperature, and ion beam composition have been systematically studied.

The films produced at the facility are currently being studied for use as dielectrics for high temperature, high voltage reduced volume capacitors; as antireflection coatings in the infrared region or the electromagnetic spectrum; and as solid lubricants. The excellent friction and wear characteristics of the films makes them particularly suited for the latter application.

### **3.2.2 Department of Energy (DOE)**

The DOE initially researched and developed IBP technologies under their nuclear fusion program. In recent years, the nuclear fusion program has not been popular and has received less support and funding. As a result, DOE has begun to explore ways to transfer this technology out of their laboratories and into the commercial sector. In addition, DOE is involved in a number of collaborative efforts to accomplish the transfer. The major commercial sector that DOE is concentrating on for the IBP technologies is the automobile industry. The IBP capabilities and initiatives of the DOE laboratories are highlighted in the following paragraphs.

#### **3.2.2.1 Lawrence Berkeley Laboratory (LBL), Berkeley, CA**

The University of California's LBL Plasma Applications Group has been working on surface coating technologies for about 12 years. Four areas of research are being pursued by the group: diamond CVD, metal ion implantation, metal plasma immersion-metal and ceramic thin films, and compact million electron-volt (MEV) ion implantation. The group developed the metal vapor vacuum arc (MEVVA) ion source which is now licensed to ISM Technologies.

The system employed by the Plasma Application Group is called metal plasma immersion ion implantation and deposition (MPIID). This technique can be used to bond materials which normally can not be bound together such as the deposition of highly adherent nickel coatings on carbon composites. The metal thin film adheres where a sputtered coating wipes off. The

MPIIID technique can also be used to coat diamond with metal, which is impossible with sputtering. Metal coated diamonds are used as heat sinks and high density mounts for computer chips.

This group has had few collaborative relationships with commercial industry. Most of their work has been government funded. ISM Technologies has licensed the MEVVA technology, but the LBL group has had no further collaboration with them.

In addition to developing of MPIIID, LBL has produced CVD diamond coatings using a microwave plasma source. They have also worked in producing amorphous diamond-like carbon (DLC) coatings. These coating processes use vacuum techniques with non-hydrogenated carbon cathodes. The hardness of these coatings can be controlled by the incident ion energy. By modulating the ion energy, a multi-layer hard and soft DLC coating can be produced. Conventional DLC coatings tend to delaminate when they get thick. Multi-layer DLC coatings can achieve much greater thicknesses at low cost.

### **3.2.2.2 Lawrence Livermore National Laboratory (LLNL), Livermore, CA**

LLNL's Chemistry and Materials Science Division addresses a variety of materials issues and problems. Modification processes include 1) ion implantations of atoms inside the surfaces of materials for creating compound and alloy layers for low concentration doping such as for

diffusion studies and calibration standards, and 2) ion irradiations for improving the adhesion of thin films, changing the stress state of surfaces and thin film structures, and studying radiation damage.

Over the last 12 years, LLNL has published a number of studies that used ion beam processing to:

- modify the reaction of materials with gases to reduce oxidation of uranium, hydrating of uranium and hydrogen permeation of iron and stainless steel
- create pure, buried compound and elemental layers
- prepare solid membrane chloride ion selective electrodes and implanted standards for various analysis techniques
- enhance the adhesion of oxide and metal coating to substrates

At present, LLNL is investigating the effects and applications related to nuclear tracking of materials and the modification of the composition at the near surface within the top nanometer of the materials.

LLNL has a project to produce gratings as large as approximately 20 inches (50 cm) in diameter using a combination of laser interference lithography and reactive ion beam etching. This strategy allows such large areas to be patterned at a relatively low cost in comparison to alternate approaches. A similar process has been demonstrated for fabricating arrays of emitter

tips suitable for electron emission-based flat panel displays.

LLNL has also conducted research and development efforts using macroparticle-free vacuum arc-based ion beams to produce coatings from intense ion beams. These efforts have resulted in the development of a commercially available source which is currently being used by a number of companies to develop new products using this technology.

### **3.2.2.3 Los Alamos National Laboratory (LANL), Santa Fe, NM**

LANL is operated by the University of California. Plasma source ion implantation (PSII) was developed for manufacturing-scale production in a, three-year CRADA established in 1992 between LANL and GM R&D Center with technical assistance from the University of Wisconsin. The goal of the CRADA was to co-develop PSII for the auto industry to improve surface hardness and wear of tooling and powertrain components. Parts supplied by the automotive industry were processed. The production of tailored surface composites was a primary goal of this agreement. Two specific applications that were targeted were nonferrous automobile parts and ferrous tools (punches and drill bits). In the CRADA, LANL has used a chamber that is approximately 15 feet long by 5 feet in diameter (4.6 meters long by 1.5 meters in diameter). The large scale PSII facility was built using previously designed technologies, including large plasma devices from DOE's

Fusion Energy Program, high-voltage technology from DoD's Strategic Defense Initiative, supercomputer models from DOE's Nuclear Weapons Program, and advanced materials R&D from DOE's Energy Research Program. Its large capacity allows hundreds of automobile parts or thousands of drill bits to be implanted in a single batch, depending of the size of the parts.

The latest facility operational at LANL is being used to examine PSII on a large scale. It can accommodate large workpiece assemblies weighing up to 10,000 lbs. The system was developed at LANL for DOE's Nuclear-Fusion Energy and Rocket-Propulsion Research Programs under the auspices of DOE's Technology Commercialization Initiative. Composition, chemistry, and microstructure will be optimized to produce improved surface properties such as wear, friction and corrosion resistance over a range of operating temperatures and in a variety of reactive environments. Emphasis is being directed towards improving tribological properties of metal surfaces. Experiments have been performed at 40kV with nitrogen plasma.

LANL has determined that though PSII is intrinsically a non-line-of-sight process, this property is only assured when the feature size is small compared to the plasma sheath dimension. Future experiments will be directed at higher accelerating voltages (up to 100kV), repetition rates (1 to 2 kHz), and with alternative ion sources such as carbon.

At present, LANL has formed a consortium with a group of OEM's, their suppliers, and Academia researchers to explore business sector opportunities. This consortium includes end users, equipment builders, system integrators, service providers, R&D laboratories, and educational institutions. Targeted business sectors include manufacturing, environmental, energy, transportation, electronics, and defense. Technology transfer initiatives are starting with component manufacturers and system integrators.

LANL researchers have successfully developed ion implantation coating techniques in medical applications to improve bone implant devices such as hip replacement joints. The theory is that the bond between the device and the bone will improve, resulting in a longer life span for the implant. LANL are custom-tailoring the synthetic hydroxylapatite (HA) coating to the titanium and have successfully bonded titanium and HA by using ion implantation.

LANL researchers are also investigating intense pulsed ion beams for materials processing. To date, demonstrated and potential applications include film deposition, glazing and joining, alloying and mixing, cleansing and polishing, corrosion improvement, polymer surface treatments, and nanophase powder synthesis. Initial experiments have emphasized thin-film formation by depositing beam ablated target material on substrates.

LANL has also been testing PSII of ammonia into electroplated chromium. They have concluded that ammonia gas (NH<sub>3</sub>) can be used

as a nitrogen source for PSII processing of electroplated chromium without risking hydrogen embrittlement. This process could potentially be used for a variety of applications.

Recently, within the last year, LANL has awarded three contracts to Institutes located in the Former Soviet Union to co-develop ion beam processing techniques for surface engineered materials, with particular emphasis on ion implantation and high-intensity pulsed ion beam deposition. These Institutes are: the Institute of Electrophysics, Ekaterinburg, the Institute of Electrophysics, Tomsk, and Nuclear Physics Institute of Tomsk Polytechnic University.

### **3.2.2.4 Oak Ridge National Laboratory ORNL), Oak Ridge, TN**

ORNL's many areas of research are in metal finishing. ORNL does not have production scale facilities, but has the capability to run bench scale studies on ion beam and other metal finishing technologies. Their facilities include a High Power Test Facility, a High Heat Flux Facility, and a Medium-Energy Test Facility. All three have been used to develop ion sources that produce hydrogen ion beams of 10 to 100A, 30 to 120 keV, for .05 to 30 seconds, and to qualify neutral beam injectors that inject neutral beams with power ranging from 100 kW to multimegawatt levels. Each of these beam facilities can be used for developing large-area ion implantation systems. Both the HHPF and the HPTF are readily adaptable to the PSII type of operation. To accomplish this, the target has

to be mounted by use of an insulating mount capable of withstanding the accelerating voltage. The assembly can then be immersed into the plasma source, which can be either electron cyclotron resonance (ECR) or RFI driven.

There are a number of ion beam studies that ORNL is involved in or has put together proposals for and are seeking out funding to support their efforts. For example, ORNL is involved in a collaborative effort with LANL to use ion plating as a hard chrome plating replacement. Magnetron sputtering would be used in conjunction with ion plating of melted chrome, which has a low hardness of about 2 gigapascals. Hydrogen and oxygen ions would then be implanted into the deposited melted chrome. ORNL representatives believe that hydrogen and oxygen impurities are what gives hard chrome its high hardness, typically 11 gigapascals. Coatings deposited by this method would probably have a thickness limit of 10 microns and would have a hardness comparable to hard chrome.

ORNL, together with ATCOM, CCAD, the University of Tennessee, U.S. Army's ARL, and ISM Technologies, studied the effects of ion implantation treatments on corrosion of aluminum in saline environment. Implanted constituents were nitrogen, silicon, titanium, and chromium. The study concluded that ion implantation of chromium is of potential practical benefit for corrosion inhibition of aluminum in high salinity environments.

ORNL is also studying high-energy ion processing of materials for improved hardcoatings. Processing techniques such as high-energy ion implantation and electron cyclotron resonance microwave plasma processing were employed on a variety of materials, including boron suboxides, a titanium-aluminum-vanadium alloy (Ti-6Al-4V), a cobalt-chrome-molybdenum alloy (CoCrMo), and electroplated chromium. The study discovered that with appropriate alloy content and other parameterization, hardnesses as great as that of electroplated chromium can be produced by nitrogen-ion implantation, at least in the 0.2 micron implantation zone.

ORNL does ion plating work using ECR microwave technology to generate plasmas. This technique is expensive, but provides excellent control of operational parameters and permits the use of a wide range of gas densities. The ECR microwave technique involves bombarding argon gas that is being acted on by a magnetic field with microwaves from above.

ECR microwave is a versatile technique and can be used as a source for both IBAD and ion plating. ORNL uses the technique primarily for semiconductor applications where the tight parametric control offered by the technique is essential. The ONRL representative mentioned that magnetron sputtering is usually preferred to ECR microwave in the U.S., but ECR microwave is widely used in Japan. It is unclear, however, what applications the Japanese have for ECR microwave.

ORNL is also seeking funding to pursue research in the area of secondary electron suppression to increase the efficiency and precision of PSII techniques. Secondary electron suppression is desirable when using PSII.

### **3.2.3 U.S. Environmental Protection Agency, Washington, D.C. and Cincinnati, OH**

The EPA is evaluating various technology alternatives to hexavalent chromium in plating and metal finishing. These include:

- Use of a nickel-tungsten-boron alloy to replace chromium
- Replacement with physical vapor deposits (chromium-titanium- and titanium-aluminum nitrides)
- Alloy deposition of hard coatings (nickel-tungsten-silicon carbide and electroless nickel-tungsten)
- Deposition of powdered chromium with an inductively coupled radio-frequency plasma torch
- Hard chromium via sputter deposition
- Chromium-free conversion coatings as a pretreatment for powder coatings.

### **3.3 Academic IBP Technology Researchers**

This section describes the R&D initiatives, and pursuits of some of the North American academic IBP technology researchers. It highlights their capabilities, current R&D efforts, cooperative teaming arrangements, funding sources, and targeted potential applications of IBP technologies. These institutions are working closely with commercial and government IBP proponents. Table 3-5 provides a snapshot view of the efforts of these institutions and their IBP technology areas of research.

#### **3.3.1 Basic Industrial Research Laboratory (BIRL)/Northwestern University, Evanston, IL**

BIRL is an industrial research laboratory at Northwestern University which develops and evaluates new or improved materials, products, and processes; producing samples and prototype production runs of materials or devices; designing and developing production-scale equipment for commercial use; and assisting and participating in the formation of new business ventures. A particular focus of BIRL's R&D is

**Table 3-5. Capabilities of Academic IBP Technology Researchers**

Academic Researchers	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
BIRL	X			X	X <sup>1,2</sup>
INRS			X		
University of Tennessee			X		
Univ. of Wisconsin	X		X	X	X <sup>1,2</sup>

<sup>1</sup> Ion Beam Mixing

<sup>2</sup> Semiconductor ion implantation

on developing materials and application processes for protective coatings to be used by industry and government for combating wear and corrosion. Researchers at Northwestern are under contract with ARPA and EPA to investigate IBP alternatives to chromium electroplating.

### **3.3.2 Institut National de la Recherche Scientifique (INRS), Montreal, Canada**

INRS - Energie et Materiaux (Materials and Energy Department) has a PSII program. It combines the expertise of two already existing groups - the plasma fusion group and the advanced materials development group. At present, this is the only team in Canada that is working in this field. The program was established in 1993 but only in this past year has more than one full-time scientist been attached to it. They currently have two full time senior scientists and two undergraduate training students.

INRS has a PSII chamber composed of a compact pulsed surface electron cyclotron resonance (ECR) source. It is cylindrical in shape with a 10 inch in length by 4 inch (25 cm length by 10 cm) in diameter chamber. Permanent magnets arranged in a checker-board pattern are used to create both the resonance surface and the confining magnetic field structure.

In addition, INRS is researching source development of radioactive ion implantation for medical applications and near-surface wear

measurements. They are exploring applications of ion beam tribological modification of surfaces which are linked to specific industrial needs in Canada. It is unclear what specific applications INRS is pursuing.

### **3.3.3 University of Tennessee, Knoxville, TN**

The University of Tennessee initiated a research program in 1986 to assess the effects of PSII of nitrogen ions on the corrosion characteristics of metals, particularly stainless steel and aluminum. Initial results in 1988-1989 indicated that stainless steel samples implanted with nitrogen ions at potentials up to 20 kilovolts increased their surface hardness by more than a factor of two, thus greatly improving their resistance to corrosion.

University graduate students use ORNL facilities for analysis of PSII exposed samples. They have been able to demonstrate improvements in the surface hardness of stainless steel and aluminum by up to a factor of 2, thus greatly improving their resistance to corrosion. Work at the University is funded by the University's Center for Materials Processing and by the U.S. Army Research Office (ARO).

### **3.3.4 University of Wisconsin (UW), Madison, WI**

UW researchers were the pioneers of the PSII process and patented it in August 1988. Up to recently, their research encompassed work in the areas of plasma physics, diagnostics, ion-material interactions' modeling, materials science issues, and a broad spectrum of industrial applications

of PSII technology. Information obtained as a result of this study indicates that UW is now researching PSII at a much reduced level of effort because of reduced funding.

UW original research in the late 1980s has to date spawned over 30 research groups worldwide that are investigating various aspects of PSII technology. UW hosted the first International Workshop on PSII in Madison, WI in August 1993. They have received funding for PSII research and have published over 60 articles in various international and national technical journals.

UW's first generation PSII system consisted of a cylindrical stainless-steel chamber 1.3 foot in length by 1.1 foot in diameter (.40 meter in height by .35 meter in diameter) with a multidipole magnet arrangement. It worked on a 2milliAmps current, a 100kilovolt voltage. The chamber was used to conduct proof-of-principle PSII experiments, demonstrate the effectiveness of PSII for a wide range of engineering materials using test coupons and, to a limited extent, in the treatment of industrial parts.

UW's second generation PSII system was a cubic meter volume chamber, with turbo-molecular, cryogenics and diffusion pumps; a gas processing system; a status control panel including a PAL 68000 (Techware) based computer; and a high voltage pulsing system.

Currently, UW is conducting PSII research using its third generation PSII system. This system is cylindrical with a length of 4 feet (1.25 meters)

and an inner diameter of 3 feet (0.90 meter). UW researchers are investigating the basic surface physics involved in the interaction of the ions and the substrate surface using this system.

UW has used the following three techniques for plasma generation: electron impact, glow discharge, and radio frequency. UW's research has demonstrated that the PSII process is capable of implanting nitrogen ions at concentrations and depths required to bring about an improvement in surface characteristics of materials.

In addition to the PSII process, UW is investigating basic plasma physics associated with the PSII process. UW is performing experimental measurements and developing theoretical models to better understand plasma sheath propagation of parts with different geometrical configurations such as cylindrical, rectangular, and cubes. This research has been corroborated by computer simulations using fluid dynamics models. The research has been utilized to better understand plasma composition and dynamics at the substrate surface.

UW researchers are employing a Monte Carlo simulation called "TAMIX." They developed TAMIX to simulate ion beam interactions and optimize PSII processing parameters. The program can be run in three modes: 1) static mode, where target composition is assumed to remain unchanged and low ion dose and damage distributions can be calculated; 2) collisional-dynamic mode for high ion dose and low target temperature cases; and 3) collisional-diffusional-

dynamic mode in situations where target temperature is high and diffusional processes such as radiation-enhanced diffusion and radiation-induced segregation are activated in addition to collisional processes.

UW's investigations on implantation-induced microstructural changes have been carried out for a wide range of materials. The objective of the research was to correlate the microstructural changes at the surface to wear and corrosion characteristics.

Field testing of PSII implanted parts has demonstrated that the PSII process has the potential to improve the wear lifetime of manufacturing tools and components such as drill bits used at the U.S. Army Rock Island Arsenal, Rock Island, IL.

In addition, the PSII technology has been demonstrated in DOD related applications. The U.S. Army Armament Research Development and Engineering Center (ARDEC) conducted research on the application of PSII on components of the electromagnetic rail gun.

In addition, UW researchers are investigating PSII as an environmentally-clean alternative to wet-bath electroplating procedures.

To date, UW researchers have conducted PSII research through the following research grants:

- An ARO grant funding research on the deposition of nitride coatings using PSII.
- A DoD Environmental Quality Grant sponsored by ARDEC and ARO to investigate PSII coatings as an

environmentally acceptable alternative to electroplating procedures.

- A program sponsored by ARO to expand ongoing PSII research by supporting additional graduate students.
- A National Science Foundation (NSF) Environmental Quality Grant to develop PSII techniques to reduce environmental hazards associated with wet-bath electroplating processes.
- A National Institute for Standards and Technology (NIST) Advanced Technology Program (ATP) to simulate and develop a mathematical model of the PSII process, and optimize PSII process parameters for specific industrial applications. The ultimate goal is to commercialize the PSII process.
- A CRADA with GM and LANL to explore potential automotive applications and industrial scale-up possibilities of PSII treated parts.
- State of Wisconsin - Applied Research Grant Program.
- Grants from private companies including General Motors, Kodak, A.O. Smith, and Akashic Memories.

### **3.3.5 Other North American Commercial and Academic IBP Technology Researchers**

In the course of this study, the NATIBO study team identified some additional North American academic technology researchers who are conducting IBP technology research. Their capabilities and/or research areas of study are illustrated in Table 3-6.

**Table 3-6. Capabilities of Other North American Academic IBP Technology Researchers**

Company	Nitrogen Ion Implantation	Metal Ion Implantation	PSII	IBAD	Other
<b>USA</b>					
Colorado State University		X			
Colorado School of Mines		X			
Cornell University			X		
Highlands University			X		
George Washington University		X			
Northeastern University			X		
University of California			X		
West Virginia University			X		
<b>Canada</b>					
Queens University	X				

### 3.4 International

In addition to the North American efforts, the NATIBO study team obtained information and data on IBP technology activities ongoing in other countries. The purpose of this section is to summarize these international activities. Appendix D contains a table summarizing international IBP technology information that was identified, grouped by country.

A preliminary analysis of the data and information obtained regarding international activities suggests that the North America may trail behind China, Russia, Japan, and United Kingdom in IBP technology research and application development. It appears that these countries have invested major financial and

manpower resources in IBP technology research and application development.

The following sections describe the IBP technology activities ongoing in China, Japan, Russia, and the United Kingdom.

#### 3.4.1 China

China has been developing PSII technology. Chinese researchers are investigating the basic physics phenomena involved in the PSII process, basic plasma diagnostic techniques, developing computer simulation models of the interactions between implanted ions and target substrates, correlate the microstructural changes at the surface to wear and corrosion characteristics. Their studies to date have demonstrated that surface properties of implanted substrates can be improved substantially.

The Chinese PSII experimental equipment, called "all orientation ion implantation," consists of a modified conventional ion coating device. Such experimental equipment has been built in Harbin Institute of Technology, Southwestern Institute of Physics, Dalian University of Technology, Sichuan University, and China Textile University. The key PSII equipment items used in the experimental devices were developed in China to include the high-voltage pulse-power supply system, the large-volume vacuum chamber and vacuum pumps, and metal-vapor vacuum arc (MEVVA) ion source. Chinese researchers have developed the three following implantation operating modes for the MEVVA ion source: ion, atom, and electron beam synchro-implantation.

One should note that Chinese researchers have developed and are using their own version of the MEVVA ion source equipment that ISM Technologies in San Diego, CA has developed and is currently marketing.

In addition, Chinese researchers are developing PSII industrial applications and preparing design information for industrial prototypes. As part of this effort, Chinese researchers are also investigating the following techniques for different industrial operations: PSII-ion beam mixing, PSII-ion beam enhanced deposition, PSII-high pressure operation, production of diamond-like carbon (DLC) films, and elevated temperature PSII implantation. The techniques are currently being used to treat aerospace bearings and components, automobile engine components, and manufacturing tools and dies.

### 3.4.2 Japan

Japan researchers and manufacturers use IBP technologies extensively in their products. Evidence of this fact is that to date ISM Technologies in San Diego, CA has sold six MEVVA-based metal ion implantation systems to Japanese firms. Information available further suggests that Japanese industry is also investing substantial funding in nitrogen ion implantation for automotive applications. Indications are that the Japanese researchers and manufacturers are not pursuing PSII.

Furthermore, preliminary indications are that Japan's Ministry of International Trade and Industry (MITI) is investing a significant funding in IBAD research and application development. Reportedly, the amount of funding is considerably more than the current North American expenditure.

Japanese researchers and industries have invested in IBP technologies for a number of reasons. First, they are getting good results in applications where coatings cannot be used. Second, IBP technologies provide a highly uniform and reproducible surface treatment, provide good quality control, improve manufacturing throughput, and minimizes scrap and re-work. Third, IBP technologies do not generate hazardous waste which requires handling and disposing and results in high remediation costs. The latter is extremely critical because Japan as a country has a relatively small capacity to handle, treat, and dispose of hazardous waste.

Furthermore, in the 1960's, Japan had a public health problem associated with cadmium as a result of illegal dumping of cadmium wastes.

It is interesting to note that the Japanese do not refer to their process as IBAD. Rather, they refer to it as ion vapor deposition. Some IBP experts in North America believe that this terminology is part of a marketing strategy designed to de-emphasize the ion beam nature of the process. Preliminary indications are that the Japanese want to de-emphasize the ion beam nature of the process because of nuclear connotations that are not well understood and may impact the commercialization of the process. This may be critical because the effect of the ion implantation process is not visible to the naked eye. Therefore the producers of ion implanted products are not able to determine if their products have been implanted or not.

MITI and industry partners have undertaken a major initiative to produce next generation nitrogen and MEVVA-based ion implantation, and IBAD equipment. This work is being conducted under the auspices of Japan's Advanced Material-Processing and Machining Technology Research Association (AMMTRA) Program. The program also includes efforts to develop laser and other advanced materials processing technologies. Funding for the AMMTRA Program is shared among MITI and the Japanese steel industry. Indications are that MITI's share of the funding for this program is estimated in the hundreds of millions of dollars.

The level of funding from the steel industry is unknown.

The NATIBO study team was able to obtain information regarding the following AMMTRA industry partners.

ULVAC Japan, Ltd. has developed a system capable of implanting ions on large surface steel sheets. Their R&D efforts have focused on developing an integrated, high-current ion beam system. It is unclear what the specific applications are for this system.

Nissan Electric Co. Ltd. researchers have developed a high-current MEVVA-based metal ion implantation system and an IBAD system to modify the surface of steels. The IBAD devices that they have developed are being used for many non-electronic applications.

Mitsubishi Electric Corporation researchers are developing ionized multiple beam IBAD technology with high deposition rates. The objective is to improve the throughput and corrosion tolerance of treated steels.

JEOL, Ltd. researchers have developed a high-current nitrogen ion implantation system for steel applications.

Kobe Steel, Ltd. researchers are modification of metal by ion implantation to improve corrosion resistance, wear resistance and surface hardness.

One should note that competing industries that are not affiliated with the AMMTRA

collaborative effort are also actively researching the IBP technology area and possible applications for their commercial products.

In addition to the AMMTRA collaborative effort, Shimadzu Corporation has developed a variable energy Radio Frequency Quadrople (RFQ) magnet that can be used to improve the transport characteristics of implanted ions for all IBP processes. RFQ magnets are capable of accelerating heavy ions with a current in excess of several milliamperes and up to energies in the million electron-volt (MeV) range.

Shimadzu Corporation's MeV ion implantation system consists of an end station, a RFQ accelerator, and an injector. They are researching potential aerospace applications for this technology such as valves for rockets and satellites.

In addition to the IBP technologies, Japanese firms are currently investigating other competing high technology surface finishing treatments. These firms include Toyota Research Lab and Mitsubishi Electric. Toyota has done substantial work with DLCs and is pursuing silicated DLCs for potential automotive applications. Mitsubishi Electric is marketing worldwide their ion cluster beam equipment and indications are that they have sold hundreds of units to date. Their process uses an ion cluster beam technique that was developed at the University of Kyoto. This technology is also being commercialized in the United States by Epion Corporation in Bedford, MA.

### 3.4.3 Russia

Preliminary indications are that Russia is the recognized world leader in the advancement of MEVVA-based metal ion implantation. Their MEVVA-based equipment is similar to those marketed by ISM Technologies in San Diego, CA.

Information obtained to date indicates that there are approximately 50 MEVVA-based metal ion beam implantation systems operational throughout Russian industry. They primarily use these systems for tool stamping and punching tools, dyes, molds, and cutting tools. The operational systems are reportedly comparable in size to the nitrogen implanter installed at CCAD. The source of the Russian IBP equipment is not known. However, given the parallel Fusion and Space programs similar to those in North America that produced the IBP equipment, the implication is that Russia is developing and producing their own IBP equipment.

### 3.4.4 United Kingdom (UK)

The UK is heavily involved in researching and using IBP technologies. They use IBP on such items as automotive components, bearings, tools, drill bits, nozzles, gears, injection molding screws, among others things. The Harwell Laboratories of AEA Technology is a predominant researcher, developer and user of IBP technologies. They have been involved in the development of IBP technologies for the past 30 years. They were one of the first companies

conducting research into the implantation of metals and the establishment of ion implantation as an industry standard process for semiconductor device fabrication.

Harwell Laboratories is considered a leader in applying the IBP technique involving a multipole source in the extracted beam or line-of-sight. Harwell has also constructed one of the largest implanters at their Harwell laboratory facility.

Another major UK IBP researcher and developer is Tech-Ni-Plant, which is the largest service center for ion implantation in Europe. They implant nitrogen ions into the surface of steel tooling, and machine parts made from steel and non-ferrous materials. They have been providing this service for the past 15 years.

## 4.0 APPLICATIONS OF IBP TECHNOLOGIES

Traditional metal finishing applications can be subdivided into the following generic areas:

*Chemically functional:* Corrosion resistant coatings, catalytic coatings, engine blades and vanes, battery strips, marine use equipment.

*Decorative:* Aesthetically pleasing coatings on all kinds of consumer products.

*Electrically functional:* Electrical conductors, electrical contacts, active solid-state devices, electrical insulators, solar cells.

*Mechanically functional:* Lubrication films, wear and erosion resistant coatings, diffusion barriers, hard coatings for cutting tools.

*Optically functional:* Laser optics (reflective and transmitting), architectural glazing, home mirrors, automotive rear view mirrors, scanning counter glass used on check-out registers such as the ones used in grocery stores, glass reflective and antireflective coatings, optically absorbing coatings, selective solar absorbers.

Ion implantation and IBAD can potentially serve most, if not all, of these traditional applications. As will be seen, many have been already demonstrated. The primary determinate in most of these applications, though, is cost. As discussed in Section 2.0, both ion implantation and IBAD are relatively high cost techniques compared to the more traditional metal finishing technologies. In order for ion implantation and IBAD to be viable alternatives in the metal finishing sector, either the peripheral costs associated with the other techniques, such as environmental remediation costs, have to be prohibitive, or high value, high payoff applications need to be identified and targeted.

Despite being unsuccessful in penetrating many of the commercial markets, ion implantation has been demonstrated for many applications. Table 4-1 highlights applications in which IBP technologies are currently in use or have been successfully demonstrated as being capable of handling or enhancing the performance requirements needed by the application. It then describes current competing technologies for the applications and the appropriate ion beam technology that could be used.

Table 4-1. Current and Demonstrated Potential Ion Beam Technology Applications

Application Area	Example Applications	Current	Demonstrated Potential	IBP Technology	Competing Technology
Medical	hip replacements, knee joints, shoulder implants, spinal screws, dental implants, optical filters, X-ray mirrors	X	X	nitrogen ion implantation, IBAD	chemical vapor deposition, physical vapor deposition,
Aerospace	ball bearings, hinge pin bearings, gear box bearings, gears, pillow blocks, turbine blades, turbine vanes		X	nitrogen ion implantation, IBAD	thermal spray, ion plating
Automotive	cylinder liners, piston rings, cam shafts, cam followers		X	nitrogen ion implantation	thermal spray, sputtering
Tools and Dies	cutting tools, punches, tool inserts, knives	X	X	nitrogen ion implantation, metal ion implantation	chemical vapor deposition, physical vapor deposition,
Non-metallic Materials	ceramic internal combustion engine components, plastics, glass		X	metal ion implantation, IBAD	

Appendix E contains tables that provide a more detailed summary of successful metal finishing demonstrations of ion implantation uncovered in research for this report. One will note that these demonstrations encompass all of the generic metal finishing application areas discussed above.

#### 4.1 Ion Implantation Applications

##### 4.1.1 Medical

The largest current use of ion implantation for commercial applications is in the medical field. Because quality of life issues are uniquely paramount in this application area, it is characterized by a willingness to pay a premium for high quality products and services. It is a high value and payoff application area that can afford the cost of ion implantation.

The pioneering work in this application area was performed by Spire Corporation in Bedford, MA, largely under the auspices of the U.S. Navy's Small Business Innovative Research (SBIR) Program. Spire currently implant nitrogen and/or carbon ions in both titanium alloy and cobalt-chrome orthopedic devices using mass-analyzed ion implantation techniques. The ion implanted medical components provide a number of benefits. Among the benefits are:

- Improved wear resistance and surface hardness,
- Reduction in particle debris from wear,
- Creation of a low friction surface,
- Enhanced bone cement adhesion,
- Improved corrosion resistance,
- Preservation of bulk material properties,
- Biocompatibility.

Examples of the ion implanted devices include hip replacements, knee joints, shoulder implants, spinal screws, and dental implants. Spire estimates that they implant in excess of 100,000 components each year.

Implant Sciences Corporation has expanded their business base and now shares a part of the medical market for some devices.

#### 4.1.2 Aerospace

The aerospace area is where ion implantation has been demonstrated on several occasions. Other cheaper, more traditional techniques such as electroplating, thermal spray, and ion plating dominate this market, and prevent ion implantation from gaining any appreciable market share. Many of the specific applications in this area require the build-up of surface dimensions that ion implantation cannot provide. Thick ion-plated aluminum coatings, for instance, are now used in various irregular shaped parts of aircraft and spacecraft as well as on fasteners. These thick ion plated coatings have even been found to be partial replacements for electroplated cadmium, and can provide good corrosion protection.

Several years ago, the U.S. Navy explored the use of ion implantation to improve the corrosion resistance of ball bearings for their jet engines. The specific ball bearings were J-79 main shaft engine bearings. This work culminated in a Manufacturing Technology program that proved that chromium ion implantation could increase the life of bearings by a factor of 2.5; that the cost to implant the bearings was less than the cost

of a new set of bearings; and that the savings from reduced overhauls, combined with reduced bearing costs, would provide a benefit to cost ratio of around 20:1. During this program the contractor, Spire Corporation, also successfully demonstrated the implantation of H-46 helicopter hinge pin bearings and helicopter gear box bearings, and also flight tested the bearings. Despite these exceptional results, though, the U.S. Navy has taken no steps to equip its jets with ion implanted bearings.

Since 1990, the U.S. Army has been exploring the use of ion implantation to improve the performance of a number of Army helicopter components. This work has been performed primarily at Corpus Christi Army Depot (CCAD). The specific helicopter components include bearings, gears and pillow blocks subject to wear and/or corrosion. To date, ground tests have been conducted with great success, demonstrating significant increases in component lifetimes. Additional tests have been conducted on the effect of ion implantation on the fatigue life of implanted components to determine if there is a possibility that ion implantation of components can lead to reduced fatigue life and potential catastrophic failure. These tests have not shown any evidence of reduced fatigue life. The Navy is actively involved and supporting the Army program.

Another potential aerospace application opportunity for ion implantation is the treatment of turbine blades and vanes. Blades and vanes used in the turbine-end of a gas turbine are subject to high stresses in a highly corrosive

environment of gases containing oxygen, sulfur and chlorine. A single (or "monolithic") material, such as a high temperature alloy, is incapable of providing both functions. The present solution in this application is to design the bulk alloy for its mechanical properties and to provide the corrosion resistance by means of a metallic overlay coating. The coating is deposited in production by electron-beam evaporation and in the laboratory by sputtering or plasma spraying. Ion implantation may be able to provide both the mechanical properties and the corrosion resistance for this application. This would also be true for turbine engines used in ground vehicles.

The Canadian DND initiated in May 1996 a trial test program of F-18 jet engine outlet "turkey feathers" nitrogen ion implanted at CCAD. The Canadian F-18 Program Office has found that they have to replace these components as many as three or four times a year. At the time of the publication of this report results of the first test trials are not available, but DND representatives are hopeful that ion implantation can result in less frequent replacement of the "turkey feathers," and therefore produce a substantial maintenance cost savings.

#### **4.1.3 Automotive**

Many researchers working in the ion implantation field believe that the automotive market will be the largest future market for ion implanted parts. The conservative nature of this market, though, is not conducive to introduction of new technologies. Competitive pressures from Japan and regulatory pressures discussed in

Section 2.0, however, may combine to make ion implantation an acceptable process in the future.

As with the aerospace market, traditional, relatively inexpensive metal finishing techniques such as electroplating, thermal spray, and sputtering dominate the present automotive market. For instance, most of the fasteners used in automobiles are electroplated, and the lightweight plastic grilles found on many cars are overcoated with chromium by sputtering to give the accustomed and acceptable appearance. The automotive market is driven more than most by decorative concerns and by cost. The competitive nature of the industry forces the automakers to budget down to the penny and the ounce in order to gain any advantage that they can.

Automotive parts that are subject to wear or corrosion are potential applications for ion implantation. However, the parts cannot be too complex, given the line of sight requirement of direct ion implantation. Cylinder liners and piston rings are examples of parts that could benefit from ion implantation. As these parts wear, they allow more oil into the engine's combustion chamber. Oil in the combustion chamber results in particulate emissions. Ion implantation of both cylinder liners and piston rings, alone or in combination with other surface treatments, could be used to increase wear resistance of these components, and in turn reduce emissions of particulates. Cam shafts and cam followers are other examples of potential applications. These parts also wear with time, reducing engine performance efficiency. A combination of ion implantation and other

surface technologies could reduce wear of these components, maintaining engine performance over the lifetime of the automobile.

Ion implantation can potentially assist in reducing the weight of automobile components as an easy way to increase gas mileage and reduce pollution. Wherever possible, automobile manufacturers are looking to substitute aluminum or magnesium for steel and cast iron. This substitution is often prevented by the fact that they do not have as good wear and/or corrosion resistance as the heavier metals that they are to replace. Ion implantation could modify the surface properties of these materials to allow them to be used.

The need in some parts of the U.S. to use alternative fuels such as methanol to reduce air pollution may also provide an opportunity for ion implantation. Methanol is more corrosive than gasoline, so while engines can burn this fuel, their internal components will not last as long. Ion implantation has been demonstrated to improve corrosion resistance of cast iron, steel and aluminum (common engine materials) and can thus be used to allow methanol-burning without design changes that would be needed to introduce new base materials such as stainless steel.

The potential of ion implantation in the automotive market was the subject of a recent Cooperative Research and Development Agreement (CRADA) between Los Alamos National Lab (LANL) and General Motors (GM). In this technology transfer arrangement,

LANL used their PSII equipment to implant a number of automobile engine components that were then tested by GM. According to GM, the PSII technique showed promise for these applications and does not have the line-of-sight limitations of DII, so was capable of implanting relatively complex parts. At the time of this report, however, PSII has not been demonstrated in a production setting. LANL now, though, has a working arrangement with Empire Hard Chrome to move their PSII equipment to Empire Hard Chrome's facility in Chicago in order to prove out the technique in a production setting. This arrangement ought to be watched very closely over the next two years to see if the potential of this technique can be realized.

#### 4.1.4 Tools and Dies

The tool and die market was the first market ion implantation researchers attempted to penetrate in the 1970's and 1980's. The high cost of manufacturing shop floor cutting tools, punches, and tool inserts was thought to make ion implantation an attractive alternative. Success in penetrating this market, though, has been mixed.

Cutting tools are made of high-speed steel or cemented carbides. They are subject to degradation by abrasive wear as well as by adhesive wear. In the latter case, the high temperatures and forces at the tool tip promote microwelding between the steel from the workpiece and the steel in the high-speed steel tool or the cobalt binder phase in the cemented carbide. The subsequent chip breaks the microweld and causes tool surface cratering and wear. At present, coatings deposited by chemical

vapor deposition or physical vapor deposition are the primary methods of protecting cutting tools. In these cases, a thin layer of a compound such as titanium carbide introduces a diffusion barrier, preventing the microwelding. Improvements in tool life by factors of 300 to 800% are possible, as well as reductions in cutting forces. Cutting tools have been implanted for some time with varying degrees of success. Generally speaking, if the material being cut is very hard, the implant will have little effect on the life of the tool. If, on the other hand, the material being cut is not particularly hard ion implantation will increase the tool life by a factor of two to five.

Molds and dies used to form plastic components, mint coinage, and generally fabricate components are regularly implanted to increase life. Two approaches are applied: direct treatment of the mold or die, and treatment of the mold or die after chromium electroplating. In this latter case, it has been found that dies and molds coated with chromium can be re-used a limited number of times after the chromium wears down by stripping off the chromium and reapplying the chromium electroplate coating. As some of these components cost over \$250,000 to manufacture, any increase in life of the chromium coating is extremely desirable. Nitrogen ion implantation can increase the life of chromium coatings by as much as a factor of ten without reducing the number of times it can be stripped and replaced. Punches are also being implanted with great success. The outer circumference of the punch is implanted. As a result, not only does one increase the life of the punch but the punch can be reground, retaining extended life without ion

implanting a second time. In fact, in some cases the punch lasts longer after the regrinding. Similarly, knives need be implanted on one side only to allow resharpening. Tests have been conducted comparing V-shaped knives implanted with carbon or nitrogen on one side against knives that are either unimplanted or coated with titanium nitride. In all of the tests, the implantation increased the life by a factor of 3.5 to 4, even after re-sharpening.

Tools inserts are a subset of the cutting tool market and have only recently begun to be implanted. Generally, the harsh conditions associated with the cutting applications where tool inserts are used - turning, grooving, drilling, threading, and milling of metals - were considered too severe for the surface effects of ion implantation to produce any improvement. A group of machinists at Corpus Christi Army Depot (CCAD), with support from the Army Research Laboratory, proved otherwise. They demonstrated that nitrogen ion implantation of both uncoated tungsten carbide and titanium nitride coated tungsten carbide tool inserts will more than double tool insert life and increase the life consistency for cutting stainless steel. Subsequently, it has been found that metal ion implantation can provide similar increases in tool life for cutting other steels, titanium alloys, cast iron, fiberglass, phenolics and a wide variety of other metals. In addition to increased life, use of implanted inserts results in faster cutting, more consistent insert performance, and better surface finish.

#### 4.1.5 Non-Metallic Materials

Ion implantation has been demonstrated to greatly increase the wear resistance of tool inserts. Most tool inserts are made out of cobalt-cemented tungsten carbide and coated with ceramics such as titanium nitride. Ion implantation improves the surface properties of monolithic ceramic materials.

While ceramic systems are simpler than metals, the highly ordered ceramic molecular structure yields some interesting results. For example, ion implantation of metals almost always results in an increase in surface hardness. In the case of ceramic materials, if the ceramic remains crystalline, the surface hardness will be increased by ion implantation. However, it is possible for implantation to make the surface amorphous, in which case the surface will become softer. In either case, the implantation results in reduced crack formation and propagation, and accordingly, reduced wear. There is also data indicating that the fracture toughness of ceramic materials is increased by ion implantation.

The most exciting results of ion implantation of ceramic materials were obtained in experiments conducted for an Indianapolis Car Racing Team by the Southwest Research Institute (SwRI) in San Antonio, Texas. The project was to find materials suitable for the high temperature engines used in Indianapolis Racing Cars. These engines operate at temperatures too high for steel or normal lubrication systems. Ceramic materials such as silicon nitride were selected for potential cylinder liners, with titanium carbide chosen for the piston rings. Without any surface

treatment, sliding tests at elevated temperatures yielded coefficient of friction values far too high for engine use.

Lubricating metals were deposited onto the surface of the cylinder liner, but those wore off in a very short time. It was only when the researchers turned to ion implantation that they were able to achieve satisfactory results. It was found that ion implantation of a titanium and nickel metallic coating on silicon nitride resulted in enormous and lasting decreases in the coefficient of sliding friction in a diesel engine environment. Clearly, ion implantation offers an excellent means of improving the properties of ceramic materials, including ceramic coatings, for engine and other applications.

Care must be taken in ion implanting ceramics. Unlike metals, ceramics are not as easily modified by gas ions. There is ample evidence that ion implantation with gas ions such as nitrogen into ceramics can lead to blistering and actual softening of the surface. This is because the gas ions can agglomerate into voids, eventually accumulating to a degree that they destroy the ceramic surface. Therefore, it is much safer to ion implant ceramic materials with metal ions.

Plastics are another material subject to surface modification by ion beams. Tests have shown that ion implantation increases the hardness of a number of plastics by more than an order of magnitude. Moreover, the peak of the hardness is not at the peak of the distribution of the implanted material, but nearly ten times that

depth. In order to cut the plastic after hardening by ion implantation of gold ions, the force on the cutting blades had to be increased six-fold.

The coefficient of friction of hard plastics can also be affected by ion implantation. Experiments indicate that the friction coefficient of hard plastic can readily be reduced by a factor of three in rolling contact by chromium ion implantation. Chromium and titanium ion implantation increases the hardness three to six times for a variety of plastics. Appropriate application of these results are still lacking, and the application to plastics offers an excellent opportunity for future development.

Ion implantation of plastics is not without its drawbacks. The most serious is the energy carried by the beam. As most plastics are poor conductors of heat and melt at relatively low temperatures, it is easy to overheat plastics during the implantation process. Thus, systems suitable for implanting metals may not be suitable for implanting plastics.

ISM Technologies Corporation in San Diego, CA worked with Oak Ridge National Laboratory (ORNL) on metal ion implantation of plastics. They found that implanting plastics with low doses of chromium and titanium leads to very large increases in surface hardness. Metal ion implantation can also be used to reduce or eliminate hydrogen embrittlement. Platinum implanted into surfaces serves as a catalyst which accelerates the recombination of hydrogen atoms into molecules so that they do not diffuse into the surface. Other implanted materials can form barriers to hydrogen as well. ISM has

investigated the use of metal ion implantation as a pre-treatment for chromium plating, which would reduce the effects of hydrogen embrittlement. Metal ion implantation has an advantage over conventional ion implantation because there is no gas loading problem. At currents of 1-2 A, there is a big problem with pumping out gas in conventional ion implantation systems. The same principle allows independent control of the pressure of deposition. The mixing of reactive gases is also much easier.

It is not well understood why ion implantation causes changes in the surface properties of materials below the implantation depth. In metal ion implantation, the implantation zone is typically 0.05 to 0.2 micrometers, whereas the implantation-affected zone (IAZ) can be as deep as 100 micrometers. ISM and other researchers have studied the mechanisms accounting for this observed effect. Understanding why ion implantation causes changes in surface properties deeper than the actual implantation depth is of interest for more than academic reasons. ISM has shown that ion implantation causes lattice defect generation in the IAZ. ISM believes that nodal dislocations probably account for the observed performance improvement of the IAZ by blocking crack promulgation at the surface. Some Russian researchers have been trying to prove this experimentally. ISM believes that there is no appreciable increase in compressive stress in the IAZ and that this probably does not account for the observed performance improvement.

Optical properties are probably the most important feature to be improved by ion

implantation of glass. The general idea is to find an implantation process that limits infrared and ultraviolet transmission without reducing visibility. Infrared radiation causes the interior temperature of closed automobiles to climb to unbearable levels. Ultraviolet radiation fades car and house fabrics and cracks leather and vinyl. The potential gains from ion implantation of glass for improving optical properties are thus quite significant, and studies are underway in both of these areas.

Another interesting area of exploration is the use of ion implantation to reduce the wear and corrosion of glass. Glass used for supermarket checkout scanners is presently being metal ion implanted to improve wear and hardness, and make the glass more resistant to scratching.

As for corrosion, generally we think of glass as being oblivious to environmental conditions. However, acidic pollutants in the air or water will attack additives in glass, resulting in structural or optical problems. It has been found that ion implantation of molybdenum will protect glass from sulfuric acid attack. It needs to be determined if such is a viable application of the technology.

#### **4.2 Ion Beam Assisted Deposition (IBAD)**

IBAD is currently used to produce thin film coatings for optical applications such as optical filters. The technique is now expanding into low friction, improved wear, and corrosion resistant coating application areas.

Applications being explored for IBAD coatings on metal substrates include corrosion protection

and many of the applications discussed above for ion implantation. As with ion implantation, IBAD has also been able to penetrate the medical market. Unique IBAD applications include the deposition of molybdenum sulfide ( $MoS_2$ ) films, and the fabrication of optical filters and multilayer X-ray mirrors.

Spire Corporation demonstrated the growth of a number of IBAD coatings under a recent SBIR contract with the U.S. Army Research Laboratory in Watertown, MA that the U.S. Army Acquisition Pollution Prevention Support Office (AAPPSSO) initially sponsored. The goal of the program was to examine the feasibility of applying IBAD to production of corrosion resistant coatings for military applications. Under this program, IBAD was investigated as an environmentally acceptable coating process to conventional plating processes using cadmium, chromium, nickel and zinc. Spire found that IBAD possesses the capability of depositing protective coatings of equivalent or superior quality to conventionally deposited coatings in a mass production environment. Specifically, Spire demonstrated the deposition of zinc, aluminum, nickel and chromium IBAD coatings. In each case, the coatings displayed performance in one or more areas that was equivalent or superior to those produced by conventional means. Additionally, all coatings were deposited with no adverse physiological or environmental effects; all waste produced by the process was in the form of solid effluents that was nearly 100% recoverable. Spire concluded that the enhanced performance, in combination with the environmental acceptability of the "dry" IBAD

process, should prompt industry to seriously consider adapting IBAD for a metal finishing production process.

Examples of IBAD corrosion protection films include silicon nitride ( $\text{Si}_3\text{N}_4$ ) films deposited on aluminum (Al) and titanium nitride (TiN) deposited on steel. In the latter case, the IBAD coating was compared with three other industrial coating processes; magnetron sputtering, arc evaporation and ion plating. The films were evaluated for composition, hardness, friction, wear and corrosion protection. The magnetron sputtered sample corroded rapidly after a few cycles. The arc evaporation coating corroded rapidly and continuously in spite of being the thickest coating. The ion plated process overheated the steel and softened it although it gave the best long term corrosion protection. The IBAD film, which was the thinnest, initially showed the lowest corrosion rate, but also eventually failed. It exhibited the lowest coefficient of friction and wear life comparable to the others. Thus IBAD shows good potential as an industrial process.

$\text{MoS}_2$  solid lubricant films deposited by IBAD have demonstrated improved performance over sputter-deposited films. They are more adherent, have longer lifetimes and are less affected by storage in atmospheres with high humidity. The major difference between sputtered films and IBAD films is that the sputtered films have a random distribution of crystalline orientations while the IBAD films grow oriented perpendicular to the substrate. This property has

the effect of making IBAD films less susceptible to damage from humidity.

Optical filters are used to protect sensors and eyes from laser radiation at specific wavelengths. Filters typically absorb light in a narrow bandwidth and transmit other frequencies, but tend to be fragile and subject to delamination under high heat loads or thermal cycling. NRL has shown the feasibility of using IBAD to deposit silicon-nitride films with periodically varying index of refraction to create what is termed a "Rugate" (as in "corrugated") optical filter. Rugate filters have been fabricated from silicon-nitride and boron-nitride materials, and filters have been fabricated for several wavelengths, including the 1.06 micron infrared (IR) laser wavelength and the 3 to 5 micron IR band.

The most impressive demonstration of the power of IBAD technology is the deposition of multi-layer films for X-ray mirrors by Japan Aviation Electronics Industry Ltd. as part of the Japan's Advanced Material-Processing and Machining Technology Research Association (AMMTRA) program on IBP technology. Performance of X-ray mirrors depends on surface and interface roughness and scattering from internal grain boundaries. Thus, it is desirable to deposit the films under conditions where interface reactions are minimized and the films are amorphous. Under the AMMTRA program, good quality X-ray mirrors were fabricated from tungsten carbide (W/C) and nickel carbide (Ni/C).

Future development of IBAD on a commercial scale will probably depend on the ability to easily

control the effects of the process variables on the properties of the thin film. Once this is accomplished, IBAD will be better able to compete in applications that presently use ion plating, vacuum arcs, and magnetron sputtering.

## **5.0 BENEFITS OF IBP TECHNOLOGIES**

The purpose of this section is to summarize the benefits of ion implantation and IBAD. Some of the benefits have been presented in the previous two sections; others are presented here for the first time. The intent is to bring together all of the benefits of the techniques into one place so that the reader can more fully comprehend what can be gained by the use of these technologies. Later in this report, market and technological barriers to commercialization of the IBP technologies are presented.

### **5.1 Benefits of Mass Analyzed and Direct Ion Implantation**

There are many benefits to using mass-analyzed and direct ion implantation for metal surface finishing. These benefits are:

- Ion implantation is an environmentally acceptable metal surface treatment process,
- Ion implantation processing costs are decreasing,
- Surface properties of implanted parts are improved,
- Surface properties can be tailored without adversely affecting bulk properties,
- Ion implantation is a comparatively low temperature process,
- No possibility of a coating delaminating,
- Ion implantation is a highly controllable and reproducible process,
- Ion implantation does not change the dimensions of implanted parts,

- Implanted parts do not require any additional rework,
- Virtually any element in the periodic table can be implanted, and,
- Ion implanted parts are biocompatible.

These benefits are discussed in more detail in the following sections. Additional benefits of using plasma source ion implantation are discussed in Section 5.2.

#### **5.1.1 Ion Implantation is an Environmentally Acceptable Treatment Process**

Ion implantation does not have any major environmental drawbacks, unlike cadmium and chromium electroplating, for instance. It does not produce any wastewater with toxic metals, does not produce any toxic fumes, and does not produce any unacceptable noise levels. All of the reactions take place inside a sealed vacuum chamber.

In the process of this study BDM attempted to compare and quantify the environmental benefit to using ion beam processing technologies as opposed to cadmium and chromium electroplating. This is not to imply that IBP technologies are to be considered direct replacements for either cadmium or chromium electroplating. Rather, the intent was to analyze the environmental costs associated with electroplating that would not be incurred with either ion implantation or IBAD. This analysis is based upon the costs associated with present and proposed regulations and on empirical data obtained on the real operating costs of 184

electroplaters in the United States. This entire analysis is presented in Appendix F of this report. The following paragraphs summarize the results of the analysis.

The goal of the first part of the analysis was to determine how much metal finishers have already spent on pollution prevention and pollution control. Based upon questionnaire responses from their member companies, the National Association of Metal Finishers (NAMF) and the Association of Electroplaters and Surface Finishers (AESF) estimate that the metal finishing industry has spent \$42 million, or 27% of capital expenditures, on pollution prevention. They further estimate that the industry has spent \$218 million, or about 5.7% of sales, on pollution control.

The study team was also able to obtain the results of a study commissioned by the National Center for Manufacturing Sciences (NCMS) on pollution prevention and pollution control technologies used in electroplating operations. This study was conducted by CAI Engineering. The study includes empirical data on real end-of-pipe pollution control equipment costs for 184 cadmium and chromium electroplaters in the United States. By analyzing the data supplied by the responding electroplaters, the average capital cost per electroplating firm for the implementation of pollution prevention and pollution control technologies was found to be \$295,025 in 1993 dollars. The average annual operating and maintenance cost for these technologies was found to be \$86,988 in 1993 dollars.

The goal of the next part of the analysis was to determine the typical cost of complying with OSHA and EPA regulations. In the case of OSHA regulations, the study team was able to acquire data on the estimated cost to electroplaters of complying with the new proposed cadmium permissible exposure limit (PEL). OSHA has estimated that compliance with the new PEL for cadmium of 5 grams per cubic meter ( $g/m^3$ ) would cost the cadmium electroplating industry as a whole \$665,400 in 1987 dollars. This represents a cost of approximately \$200 per plant and \$78 per employee, or 7.59% of the profit of the average electroplating shop.

As for EPA regulations, data was acquired from EPA on the estimated cost of complying with the Phase I Metal Products and Machinery Rule for both direct and indirect dischargers. Under EPA's preferred option for direct dischargers, EPA has estimated that compliance with Phase I would cost the industry as a whole \$59 million in capital costs and \$13.1 million in annual operating and maintenance costs. The average cost to an affected facility would be \$5,600 in capital costs and \$1,200 in annual operating and maintenance costs. Under EPA's preferred option for indirect dischargers, EPA has estimated that compliance with Phase I would cost the industry as a whole \$337 million in capital costs and \$145 million in annual operating and maintenance costs. The average cost to an affected facility would be \$31,800 in capital costs and \$13,700 in annual operating and maintenance costs. All these costs are expressed in 1989 dollars.

Data acquired from IBP researchers as part of this study indicates that the start-up capital costs for installing a small-scale nitrogen implanter range between \$250K to \$500K. The above analysis indicates that these capital costs could be almost fully covered by money now spent to remediate potential environmental problems at electroplating plants. The analysis also indicates, though, that the surface finishing industry as a whole, and the electroplating industry in particular, has already made significant investments in environmental remediation, and continues to do so. This may partially explain why many metal surface finishers are unwilling to invest in IBP technologies; they do not want to see their already substantial investments in environmental remediation to have been in vain.

### **5.1.2 Ion Implantation Processing Costs are Decreasing**

As in any other surface finishing technology, costs for ion implantation will fall as equipment capacity increases. Direct ion implantation systems, such as the metal ion implantation systems built by ISM Technologies and the nitrogen ion implantation systems built by Implant Sciences and installed at CCAD, are versatile, relatively simple and cheap to operate. No large extractor magnets are necessary as in the case of MAII systems. Also, in direct metal ion implantation, no large volumes of gas need to be dealt with by the pumping system. With the advent of industrial scale direct metal ion implantation systems, ISM states that costs have fallen from the order of \$1-\$10 per square centimeter ( $\text{cm}^2$ ) to as low as \$0.03 per  $\text{cm}^2$  and will drop to below \$0.01 per  $\text{cm}^2$  in equipment

now under construction. In their paper "Cost Estimates for Commercial Plasma Source Ion Implantation," Alexander and Rej also estimate that a reasonably sized PSII treatment facility should be able to treat a surface area of 10,000 square meters ( $\text{m}^2$ ) per year at a cost of \$0.01 per  $\text{cm}^2$ . If these prices can be achieved, ion implantation will be able to directly compete cost-wise with the traditional surface finishing techniques such as electroplating.

### **5.1.3 Surface Properties of Implanted Parts are Improved**

Ion implantation has been demonstrated to improve corrosion and wear resistance; increase surface hardness; and lower the coefficient of friction, or increase lubricity. In addition, the surface finish of treated parts are not affected, an important consideration for decorative applications. In fact, in most cases the surface finish is improved because of the cleaning action of the ion beam (See Table 2-1).

### **5.1.4 Surface Properties can be Tailored Without Adversely Affecting Bulk Properties**

Since ion implantation only affects the top 1 to 100 microns of any metal surface, important inherent material properties of the piece being implanted are largely unaffected. The actual impact zone of the implant is limited to a depth of 0.2 microns, as will be discussed later in the report. The actual impact zone is the area where the ion beam impinges on the surface and where the chemical reaction between the ion beam and the surface is a maximum. In the medical application area, for instance, the excellent mechanical and chemical properties of titanium

alloys are preserved and complement the improved properties provided by nitrogen ion implantation.

#### **5.1.5 Ion Implantation is a Comparatively Low Temperature Process**

Ion implantation typically takes place at temperatures less than 300 degrees Fahrenheit (°F) or 150 °C. This can be compared with PVD, which takes place between 400 and 950 °F (200 and 510 °C), and CVD, which takes place between 1750 and 1950 °F (950 and 1065 °C). This comparatively low processing temperature allows ion implantation to be used on materials, such as plastics, that might otherwise be damaged or destroyed when exposed to high temperatures.

#### **5.1.6 No Possibility of a Coating Delaminating**

Ion implantation is a surface modification technique only. It is not a coating technique. Thus, there is no coating to potentially flake off or delaminate. The implanted ions do react chemically with the atoms of the piece being implanted but this reaction takes place within the surface of the piece and acts to improve wear and corrosion properties.

#### **5.1.7 Ion Implantation is a Highly Controllable and Reproducible Process**

This is the primary reason ion implantation is used in the semiconductor field. The ion species, ion energy, implantation dose and ion current density can be precisely controlled, resulting in high quality implants with the exact properties

required. Research is still necessary to determine precise control parameters for particular applications. This is not a limitation of the process, though, but rather a gap in knowledge.

#### **5.1.8 Ion Implantation Does Not Change the Dimensions of Implanted Parts**

As stated previously, ion implantation is a surface modification process. It is not a coating process. Thus, the dimensions of a part being ion implanted do not change as a result of the ion implantation process. This property is actually both a benefit and a limitation. On the benefit side, costly redesign of existing components is not required to use ion implantation. They can be ion implanted and then placed back into operation without concern that the dimensions of the part may have been modified. As mentioned in Section 3.0, though, many wear applications require the build-up of surface dimensions to protect the substrate. For these applications, part specification changes would be necessary to use ion implantation.

#### **5.1.9 Implanted Parts Do Not Require Any Additional Rework**

Parts often have to be ground or polished after having surface treatments applied to them, leaving behind substantial wastes that need to be disposed. This post-treatment rework is not required for parts that have been ion implanted since ion implantation does not apply a coating to parts being treated. It is also not required after physical vapor deposition treatments. Boeing has prepared a cost-benefit analysis for chromium electroplating and its alternatives that indicates that post-plate grinding and masking,

which are unnecessary when using IBP technologies, can represent nearly twice the cost of waste treatment and disposal.

#### **5.1.10 Virtually Any Element in the Periodic Table can be Implanted**

As mentioned in Section 2.0, virtually any element can be ion implanted. This is more important for applications other than metal finishing applications that use MAII, but it does offer the promise of the development of exotic metal compounds that provide specific, otherwise hard to produce performance properties.

#### **5.1.11 Ion Implanted Parts are Biocompatible**

This property is particularly important for the medical application area. Medical devices ion implanted using MAII are not known to have an abnormally high body rejection rate.

### **5.2 Additional Benefits of PSII**

In addition to the above benefits, there are also advantages specific to the use of PSII. These benefits are:

- PSII allows non-line-of-sight processing,
- Workpiece manipulation is not required, and,
- PSII promises faster throughput than either mass-analyzed or direct ion implantation.

These additional benefits are discussed in the following subsections.

#### **5.2.1 PSII Allows Non-Line-of-Sight Processing**

As one will see later in the report, MAII and DII are limited in the complexity of the parts that can be implanted due to the line-of-sight nature of these techniques. The unique "workpiece as negative electrode" basis of PSII allows for non-line-of-sight processing.

#### **5.2.2 Workpiece Manipulation is Not Required**

This benefit is related to the non-line of sight processing advantage of PSII. The schemes used most often in MAII and DII to work around the line-of-sight requirement involve the design of rotating turntables and other workpiece manipulators to put more of the surface of the part in the ion beam. Such manipulation schemes, though, add to the cost of MAII and DII. The "part as negative electrode" basis of PSII alleviates the need for such schemes.

#### **5.2.3 PSII Promises Faster Throughput Than Either Mass-analyzed or Direct Ion Implantation**

The high currents used in PSII translate to more ions impinging on the workpiece being implanted within a set amount of time than either MAII or DII. Thus, PSII has the potential to provide faster throughput than either of the other implantation techniques, resulting in lower processing costs. One must be cautioned, though, that at the time of this report PSII has not been demonstrated in a production setting.

### **5.3 Benefits of Ion Beam Assisted Deposition**

As mentioned in Section 2.2, IBAD is a hybrid of ion implantation and PVD. It combines the advantages of both techniques. These benefits are:

- IBAD is a comparatively low temperature process,
- IBAD coatings exhibit high adhesion,
- There is no inherent coating thickness limitation,
- IBAD coatings exhibit higher density than traditional coatings,
- IBAD is a highly reproducible process, and,
- IBAD allows precise modulation of composition with depth.

These advantages of IBAD are discussed in more detail in the sections that follow.

#### **5.3.1 IBAD is a Comparatively Low Temperature Process**

Like ion implantation, IBAD takes place at low temperatures. Even polymers with low melting points can be coated, because the deposition temperature can be maintained between room temperature and about 100 degrees Celsius.

#### **5.3.2 IBAD Coatings Exhibit High Adhesion**

Parts that are coated using IBAD can be sputter cleaned as with PVD with the ion source that is part of the IBAD system prior to coating deposition. This promotes improved bond formation between the part and the coating. The ion source also acts to continuously clean the

surface during coating deposition, further improving the adhesion. The adhesive strength of IBAD coatings are typically 10 to 100 times higher than for coatings deposited by PVD.

#### **5.3.3 There is No Inherent Coating Thickness Limitation**

Most deposited coatings retain stress that limits the thickness that can be deposited. The stress can either rupture the interface bonds between the part and the coating or exceed the cohesive forces of the material, forcing delamination or destruction of the coating. Research has shown that IBAD coatings can be grown with very small stresses, resulting in no inherent limitation on the thickness of IBAD coatings.

#### **5.3.4 IBAD Coatings Exhibit Higher Density Than Traditional Coatings**

Traditional coating techniques such as electroplating and thermal spray leave voids or columnar structures that allow contaminates and corrosives to reach the underlying substrate material that the coating is there to protect. IBAD coatings have been found to be higher density than many of the more traditional techniques, thereby reducing the number of voids.

#### **5.3.5 IBAD is a Highly Reproducible Process**

Like ion implantation, IBAD has developed into a highly reproducible process with the precise control of ion source and beam standard operating procedure.

### **5.3.6 IBAD Allows Precise Modulation of Composition with Depth**

The IBAD coating can be precisely modulated as a function of thickness to produce functionally gradient materials with properties such as graded hardness, coefficient of thermal expansion, refractive index, density, tensile strength, and stress. In other words, IBAD coatings can be grown so that the value or strength of these properties changes as you probe deeper within the coating.

## **6.0 BARRIERS TO COMMERCIALIZATION**

### **6.1 Socio-Economic or Market Barriers**

The following sections describe the socio-economic and market barriers to the further commercialization of the IBP technologies that we identified in the conduct of this study. The barriers are not intended to be all inclusive; however, they represent the most prominent and influential ones we identified during the conduct of this study.

From a socio-economic and market perspective, the primary barriers are related to the current financial burden associated with acquiring and operating IBP equipment, and the nature of the technologies. Other barriers are based upon perceptions that were fostered during the initial commercialization of the IBP technologies in the 1980's. Both types of barriers are discussed in the following sections.

#### **6.1.1 IBP Technologies Require High Capital Investment Cost**

Historically, the biggest barrier to the wider adoption of IBP technologies in the metal surface finishing industry has been high capital start-up costs. Typical mass-analyzed systems, for instance, can cost upwards of \$2M, not including additional overhead costs for items such as test equipment, and facility costs such as rent and electricity. Estimated capital costs for a hypothetical PSII business are still \$2.74M;

\$860K for the high voltage system, \$1.48M for the vacuum system, and \$400K for "ancillaries," which include \$200K for a machine shop, overhead crane or gantry, air compressor and cleaning equipment, and \$200K for laboratory capital equipment such as a residual gas analyzer, oscilloscopes and other electronic diagnostic apparatus, a chiller, and a surface hardness tester.

The metal finishing industry sector is comprised primarily by small businesses. It is difficult for the small businesses to absorb the capital costs needed to acquire IBP related equipment and presents a financial burden to these companies.

The high capital costs also present a financial burden to large, diversified companies. These companies base their capital investment on projected return on investment (ROI) over a two or three year timeframe. The current lack of high volume, high value applications makes it questionable whether a reasonable ROI can be achieved in this timeframe under the market conditions.

Some entities within the metal finishing business and end-users believe that the costs associated with nitrogen and MEVVA-based metal direct ion implantation are similar to the costs for mass-analyzed ion implantation and PSII. However, such is not the case. Small-scale nitrogen and metal ion implanters currently cost between \$250K and \$500K (US). The financial situation and the size of the company will determine if the current cost to acquire a small-scale nitrogen or metal ion implanter presents a financial burden.

In conclusion, the reality of high capital investment for nitrogen and MEVVA-based metal direct ion implantation technologies could be more a perception than a reality.

The real issue now is no longer if companies can afford the capital costs of these systems, but whether they should in order to maintain their competitive posture within the commercial and defense industrial base. The answer to this question is now more dependent on the ability of the IBP service providers to effectively market these technologies for the application areas that show that greatest potential, rather than end-users being able to afford the treatment. As with any investment, if the investment in IBP technologies can prove to have reasonably high return, such as the market grows for the IBP technologies, the amount of the initial capital costs should not be the issue that prevents firms from acquiring an IBP technology equipment and capability.

#### **6.1.2 IBP Technologies Processing Costs are High**

The perception of many end-users not familiar or up-to-date with IBP technologies is that the cost of using them is expensive compared with other metal surface finishing techniques. In some cases, this perception is based upon costs that were quoted by IBP service providers for particular applications during the very early marketing of the technologies in the 1980's. The prices quoted during that period were invariably based upon the use of expensive mass-analyzed systems that used magnets to analyze and direct

the ion beam, and also separate out impurities, and were two orders of magnitude larger than present costs.

The development of newer nitrogen and MEVVA-based metal ion direct ion implantation systems has resulted in lowering the processing costs. As mentioned in Section 5.0, the costs of using the techniques have fallen by a factor of 10 since the introduction of the technologies, and further reductions by an additional factor of 10 or more are foreseen by some of the present service providers. If the expected reductions materialize, costs of the IBP technologies will be on par with other metal surfacing techniques.

As with the capital costs discussed in the previous section, high processing costs associated with IBP technologies are currently more of a perception rather than a reality.

#### **6.1.3 IBP Technologies Have Higher Labor Costs Than Traditional Metal Surface Finishing Techniques**

Many potential IBP technology users believe that highly trained and educated scientists and engineers are required to operate IBP equipment. This perception stems from the fact that the technologies were originally developed in DOD, DOE and academic laboratories. Thus, the belief is that the labor costs for commercial IBP systems is higher than the labor costs for more traditional metal finishing techniques. This is because commercial firms would have to hire

these highly trained scientists, engineers and technicians to operate the IBP equipment.

In the case of PSII, this perception may be partially true. In PSII systems, higher currents are used, and there are critical safety concerns related to the generation of x-rays and the residual charge left on the pieces that have been implanted. High priced, high voltage electronics and safety technicians may be required to operate these systems.

Based upon data available to date, the application of PSII technology to a production environment may or may not have higher labor costs depending on the need for highly trained and educated operators. Thus, the PSII business arrangement between LANL and Empire Hard Chrome in Chicago, IL will have to be observed closely to see what additional labor costs, if any, are incurred when applying PSII techniques in a production environment.

For nitrogen and metal direct ion implantation the perception of high labor costs may be a false perception. CCAD, Implant Sciences, and ISM Technologies have demonstrated that both of these processes can be performed in a "cookbook" fashion with trained machinists using menu-driven control software. The issue now has more to do with developing the required ion implantation recipes for specific applications and modularizing current control software to accept the new recipes.

#### **6.1.4 IBP Technologies are Harmful, and Difficult to Understand and Implement**

Ion beam techniques are perceived by many to be harmful, esoteric, and difficult to understand and implement. The images most conjured up by the term "ions" or "ion beams" is one of nuclear weapons, or a futuristic battlefield with soldiers equipped with laser and ion beam weaponry that burns holes through flesh or advanced armor, or even of a space-based defense that utilizes satellite based laser and ion beam weapons to destroy incoming attacking missiles. Preliminary indications are that a Japanese firm that is marketing IBP technologies worldwide for automotive applications does not use the term "ion beam" when describing its products and services for the reason stated above.

Another image is of the lone researcher huddled in his dark laboratory peering into a vacuum chamber, constantly fiddling with knobs to get just the right settings.

A corollary to this perception problem is the issue many have with not being able to "see" an implant. With the more traditional techniques such as electroplating or thermal spray, one can see that something has happened to the part that has been coated; the dimensions or the color of the part has changed, or the part is slipperier to the touch. Companies that are in the ion implantation business sometimes have to convince customers or potential customers that they have actually done something to the part they have implanted.

The truth is more mundane. On more than one occasion, potential end-users of IBP technologies indicated that they do not understand the science of IBP technologies, and that they probably couldn't understand it. If they couldn't understand it, there was little chance that they would try to implement it for their specific application.

#### **6.1.5 Development of Low-Cost Environmental Remediation Techniques for Traditional Metal Surface Finishing Techniques**

Companies that provide traditional metal surface finishing services understand the need to be more diligent in remediating the hazardous waste from pollution producing processes such as electroplating. Thus, these companies have invested in the development of procedures and technologies that make their operations less of an environmental hazard. In most cases, these environmental technology fixes are much less costly than implementing IBP technologies. The results are cadmium and chromium electroplating plants that are essentially "zero-discharge." That is, none of the heavy metal waste is released into the municipal water supply or the environment. The waste is either recycled in the plant itself, or is collected in solid form with filters or other devices, and then disposed in specially designated hazardous waste landfills.

If the traditional lower cost metal surface finishing service providers can continue to provide their products in an environmentally safe

fashion, the environmental argument for using IBP technologies becomes irrelevant. End users can continue to rely on the techniques that they have always used, and that they both trust and understand. The marketing job of the IBP technology service providers then becomes one of making their case based upon the cost and performance of their treatments alone.

#### **6.1.6 Market Conservatism**

The manufacturing industry in the United States and Canada is conservative in outlook and is often resistant to the introduction of new methods, particularly high technology methods such as ion implantation and IBAD. This is particularly true in the metal finishing industry because of the number of other alternative technologies that already exist and have already been put into commercial practice (See Table 2-1). Many potential customers turn away from IBP technologies even after successful demonstrations as a result of other factors discussed in this report, most predominantly capital and operating costs.

There have been numerous unsuccessful attempts to establish an IBP technology industry presence in the U.S. since the early 1970's. Zymet, Ionic Atlanta, Ion Surface Technologies and Omni Implantation are all companies that have failed in attempts to market IBP technologies for metal surface finishing applications. These companies failed because they were unsuccessful in finding appropriate applications for the IBP technologies. With the number of commercial

failures in this technology area, end users are justifiably wary of becoming dependent upon the technology to meet their requirements.

#### **6.1.7 Production Priorities**

For many companies who produce metal or steel products, wear of tools or corrosion of components is not necessarily the most important production priority. In some cases, such as the hand tool industry, the improvement of these properties will mean that companies may sell fewer of their products because of the increased life expectancy of the tools.

Highly competitive industries such as the hand tool industry will be very reluctant to embrace technologies that ultimately affect their number one priority, which is selling more hand tools. In addition, these industries are often very sensitive to changes in decorative properties, which may be modified by ion implantation or IBAD.

#### **6.1.8 Need for Specification Changes**

Specifications for existing parts define the characteristics, dimensions and tolerances. If a coating is used, such as an electroplated or a thermal spray coating, the specifications will fully designate the thickness of the coating. Specifications may also stipulate the metal surface finishing process to be used to treat the part. They may detail the exact electroplating or CVD chemistries.

In any of the above cases, specifications would have to be changed or waivers granted to use IBP technologies or industry will have to develop a commercial specification. For instance, in an analogy to the latter, the cadmium electroplating industry is in the process of adopting a commercial standard that will replace existing military specifications.

Since the specification change process is long and laborious, the adoption of a commercial IBP technology standard will be the preferred course of action under the current DoD Acquisition Reform Initiative. However, the adoption of a commercial standard will still require extensive and conclusive testing to prove the IBP technologies viability for the specific application.

### **6.2 Technical Barriers**

The following sections describe technical barriers to the further commercialization of the IBP technologies.

#### **6.2.1 IBP Technologies are Line of Sight Processes**

Direct metal ion implantation and nitrogen ion implantation, as well as IBAD, are line-of-sight processes. The surface being implanted has to be in the line of the ion beam to be properly implanted. This limitation means that workpieces need to be manipulated in some manner during the implantation process, that the ion beam needs to be rastered, or that multiple ion sources need to be used so that all surfaces

are implanted. In the case of the nitrogen ion implanter located at CCAD, these manipulations are done with the use of a rotating platen. These manipulations or additional features add cost to the process, particularly for large or heavy items. PSII shows promise in overcoming this limitation, but this technology is still in its commercial infancy.

In addition, treating interior surfaces of tubes or pipes is virtually impossible for ion implantation. Even with PSII, it is difficult to treat interior surfaces where the depth to diameter ratio is greater than one. There are many areas where this is inadequate, such as the nozzles for water jet cutters.

#### **6.2.2 Size of Vacuum Chambers**

The size of the present vacuum chambers limits the capability for treating large parts, components, and tool pieces, and also limits batch sizes for small items. The largest nitrogen ion implantation system presently being used in a production environment is the 6 feet long by 4 feet in diameter (1.8 meters long by 1.2 meters in diameter) chamber at Corpus Christi Army Depot (CCAD). This system can simultaneously process up to 500 tooling inserts of various geometrical complexities and sizes in one batch. The largest metal ion implantation system in North America is a 6.5 feet long by 5 feet in diameter (2 meters long by 1.5 meters in diameter) system produced at ISM Technologies in San Diego. Preliminary indications are that

Russia may have a larger metal implantation system in operation.

A 12 feet long by 6 feet in diameter (3.6 meters by 1.8 meters) system is scheduled to be installed by Implant Sciences Corporation at the National Defense Center for Environmental Excellence (NDCEE) in Johnstown, PA in the Fall of 1996. This system is not being designed for long-term large scale production, but rather to demonstrate the environmental benefits of using ion implantation and IBAD.

Most of the IBAD systems that exist in government, industry, and university laboratories are designed for sample sizes with diameter less than 1.2 inches (30 mm). These facilities are able to perform depositions on a small scale for limited batch sizes. Many applications require large areas to be coated. Systems that can handle workpieces with a 40 inch (1 meter) diameter have been built. Since non-optical applications do not require strict film uniformity, very large areas could be coated using existing equipment by the routine manipulation of the workpieces.

#### **6.2.3 Testing**

The problem with testing parts that have been ion implanted or have had IBAD coatings applied is duplicating in the laboratory the conditions that the actual components see in use. In many cases, it is extremely hard to even determine the conditions. Even if a particular wear environment can be duplicated, realistic tests can take years to run, particularly for mild wear

applications. Thus, improvements in testing methods are needed before the ion implantation process can be accepted for many applications.

#### **6.2.4 Implantation Non-uniformity**

The effectiveness of ion implantation is dependent upon the angle at which the ion beam impinges on the surface being implanted. The optimum implantation angle is 90 degrees, or normal to the workpiece. If a part has a particularly complex geometry, the implanted ions may not be a uniform dosage throughout the workpiece. Some ions may be implanted at one depth; others at another depth. This is particularly important for flight critical aerospace applications and for medical applications because the non-uniformities will cause uneven wear and potential failure of an item. This problem is not as important for steels implanted with nitrogen, but is believed to be critical for other materials such as stainless steels and titanium alloys.

#### **6.2.5 Shallow Penetration Depth**

As has been mentioned, ion implantation is a surface modification technique; it does not affect properties of the substrate material. As such, it only affects properties to a very shallow penetration depth. In the case of nitrogen ion implantation, the implantation zone (see Section 5.1.4) depth is typically less than 0.2 microns. The effect of this shallow penetration depth is that nitrogen implantation can only overcome "mild" wear phenomena as opposed to "severe"

wear phenomena. The severity of the wear will depend upon the application and the operational environment.

#### **6.2.6 Optimum Ion Implantation Parameters**

There is still a large area to be explored in regard to optimum ion implantation parameters, including ion species, ion energy, implantation dose and ion current density. Most research on ion implantation has been done at parameters that reflect the available equipment, not the optimum parameter range or a specific application. For instance, a significant amount of work has involved ion implantation with beam energies in the million electron volt range. While the results have been quite good, the energy is too high for production work.

New equipment is now available, such as the MEVVA metal ion implantation systems, and new processes, such as PSII, that open new areas for exploration with excellent prospects for production. Analysis needs to be done of their applicability, and appropriate specifications written such that a designer needs only to call out a process, rather than spelling out the details of the implantation.

#### **6.2.7 Implantation Mechanisms**

There is a great deal of disagreement among IBP researchers regarding the mechanism by which ion implantation increases the wear resistance of materials. This is partly because the mechanism

is not the same for all wear systems. It is also because testing is extremely difficult (as mentioned above), particularly in mild wear applications. Improvements in this area could lead to more information on the mechanisms, and extend applications much further.

## **7.0 Conclusions**

This section presents conclusions based on information gathered throughout this study effort and based upon the information presented in the preceding sections of the report. The conclusions are based on observations of the current technical and business environment associated with the IBP technologies.

### **7.1 Ion Implantation is a Mature, Environmentally Safe Process**

Mass-analyzed ion implantation has been used for more than 30 years in the semiconductor electronics industry. It is the only process capable of providing the pure dopants required for semiconductor processing in a precise and controllable fashion. The technique is used throughout the world for both basic research and production scale batch processing, and does not produce any toxic emissions.

Direct ion implantation of nitrogen and metals are less matured technologies than mass-analyzed ion implantation (MAII). They are also simpler, since neither technique requires the analyzing magnets that are critical for the precise control of MAII systems. Direct ion implantation of nitrogen and metal technologies are also now used worldwide to improve the wear and corrosion performance of many metal and steel components.

### **7.2 Plasma Source Ion Implantation and IBAD Require Additional Study and Demonstration**

PSII and IBAD can potentially overcome many of the limitations that are inherent in mass-analyzed and direct ion implantation. As examples, PSII can overcome the line-of-sight processing limitation, and IBAD can overcome the build up of surface dimensions limitation. However, both of these technologies lack commercial maturity.

PSII had its genesis in the nuclear fusion program. The characteristic high beam fluences promise very high throughputs but also present critical safety issues. PSII systems require shielding against x-rays, and operators must be trained to recognize and mitigate the charge build-up on pieces being treated.

IBAD was developed as a means to overcome the penetration depth technical limitation inherent in ion implantation. The technique is perhaps 5 to 7 years behind ion implantation in terms of maturity in the metal surface finishing area. However, it has already become a standard technique for depositing optical thin films on optical lenses and mirrors.

### **7.3 IBP Technologies Have Not Achieved Wide Acceptance for Metal Surface Finishing Applications in North America**

Unlike the semiconductor industry, which is exclusively dependent on ion implantation to

provide the required performance properties, the metal surface finishing industry is characterized by a wide assortment of commercially proven technologies (See Table 2-1). The IBP technologies are faced with much stiffer competition in the metal surface finishing sector as opposed to the semiconductor sector. The pool of potential metal finishing applications is large, but the number of metal finishing techniques is also large. Therefore, none of metal finishing techniques has a predominant market share.

Presently, the only sizable market penetration for IBP technologies in North America has been in the medical sector. This sector is characterized by a willingness to pay a premium for high performance surface treatments. Other markets shy away from IBP technologies because of cost concerns, the mechanisms for IBP technologies effectiveness is not well understood, and other concerns both market and technology oriented such the barriers described in Section 6.0.

In the U.S. marketplace, some customers are wary of ion implantation technology because the mechanisms responsible for its effectiveness are not well understood. This may be one of the reasons that ion implantation has not been widely accepted in the U.S.

#### **7.4 Direct Ion Implantation of Nitrogen and Metal Ions are Technologies that are Ready NOW for Metal Surface Finishing Applications**

CCAD, SwRI, Beamalloy, Implant Sciences, ISM and Spire have all successfully

demonstrated nitrogen and metal ion implantation for numerous applications such as aerospace bearings and automotive pistons. Easy to use, menu driven control software has also been developed for these technologies that enables standard machinists to operate the equipment. These technologies are ready to compete with the other commercially accepted metal surface finishing techniques.

#### **7.5 Far Eastern, Russian and European Markets are Currently the Most Viable Markets for IBP Technologies**

Japan, Russia and the European countries have been more aggressive in embracing the IBP technologies, either for environmental reasons or because they recognize the long-term potential of the techniques.

Many of these countries, particularly Japan, make substantial initial investments to foster emerging technologies that have wide future applicability. This reflects a philosophical difference with the way U.S. and Canada typically approach emerging technologies, where both government and industry expect relatively rapid return on any technology investment. The Japanese government and industry have made a commitment to develop IBP technologies, as evidenced by the AMMTRA Program and the increasing use of the technologies by the Japanese automakers.

## **7.6 The Financial Investment for IBP Technologies is Presently Considerable and Risky**

In the highly competitive metal surface finishing sector, any investment made by a company into relatively complex and expensive technologies such as the IBP technologies represents an enormous risk. In particular, when the technology does not presently have a sizable existing market or a demonstrated potential to capture a sizable market.

When measuring the risk, the IBP technologies need to be evaluated within the perspective of the overall metal surface finishing sector. In particular, their market potential needs to be measured against the assessed needs of end users and the capabilities and limitations of the numerous other metal finishing alternative techniques.

## **8.0 RECOMMENDATIONS**

This section presents recommendations to the DOD and Canadian DND. These recommendations are designed to overcome the market and technical barriers discussed in Section 6.0, and address appropriate conclusions presented in Section 7.0.

The recommendations define specific actions that could be undertaken to foster the advancement and successful incorporation of IBP technologies, and ensure the dual-use of these technologies within the North American commercial and defense industrial bases.

### **8.1 Develop Additional IBP Metal Surface Finishing Capabilities within the DOD and DND Sustainment Communities**

The IBP metal surface finishing capability developed at CCAD has demonstrated the utility of the technologies within the U.S. Army community for a specific set of defense applications as it relates to aviation components and shop tools. The time is appropriate to consider expanding both the defense using community and the breadth of applications. The DoD and DND Sustainment Communities provide excellent potential proving grounds for this expansion.

As a first step, take advantage of the fact that the IBP technologies are environmentally clean technologies. DOD and DND could selectively target those depots and logistics centers that

presently perform pollution producing processes such as cadmium and chromium electroplating and educate key personnel at the sites on the benefits of the IBP technologies, and promote the technologies for appropriate applications. Depending upon the interest shown and the potential applications identified, an additional depot or logistics center could be chosen to have an implanter installed to demonstrate a wider range of applications. Depending upon the targeted applications, DOD and DND could select to fund the acquisition and installation of different types of equipment such as direct nitrogen implanters, direct metal implanters, PSII implanters, or IBAD systems at different sites. One should note that this approach is similar to Japan's AMMTRA Initiative described in Section 3.4 of this report.

In addition to increasing the user community and expanding the breadth of applications, this recommendation has other benefits. First, the expectation is that proven and publicized defense applications will translate to generally wider acceptance of the technologies in commercial application areas. The wider acceptance will itself translate to a larger and more stable market base for companies, leading to a less riskier investment climate for the IBP technologies. In effect, the depots and the logistics centers would be sharing the financial and technical risk burden with the companies willing to invest in the technologies. Second, the process of educating more people of the benefits of the IBP technologies will assist in forming more realistic perceptions of the technologies.

## **8.2 Develop a Near-Term IBP Technology Insertion Program**

A widely applicable, high volume or high payoff, near-term dual use success of IBP technologies would produce an enormous benefit. Cost reductions resulting from economy of scale would be widely demonstrated and the IBP technologies would gain wider acceptance. DoD and DND might consider investing in a developmental application that is widely applicable and has high potential payoff.

Since PSII and IBAD are currently less matured technologies, an application should be targeted for which either nitrogen or MEVVA-based metal ion implantation is appropriate. Wear applications in the automotive industry are one potential application area. High temperature and corrosive applications in the aerospace industry are other potential areas that meet the criteria.

The first step in the program should be a thorough survey of the pressing wear and corrosion problems in the two industries. This should be accomplished in conjunction with both the end users and the IBP technology equipment and service providers. Inclusion of both parties will ensure that all issues are fully addressed and understood, and will also foster an environment for sharing data and information.

Once an application is chosen, the defense and industry partners should together develop a technology insertion plan, and agree upon measurable surface treatment cost and

performance goals and objectives. The intent would be to have quantified cost and performance measures at the completion of the effort that can be compared against the traditional surface finishing method or methods such as those found in Table 2-1, being used for the application.

## **8.3 Ensure Adequate Funding and Management Oversight of IBP R&D Efforts to Overcome Technical Barriers**

The U.S. Army's ARL has two existing Basic Science programs and two Exploratory Development programs whose scope includes investigation of the basic science and applicability of the IBP technologies. The U.S. Navy's NRL has an existing MANTECH program with similar scope.

DoD and DND could ensure adequate funding for the IBP R&D efforts to understand the gaps in knowledge associated with the technologies' basic scientific mechanisms. A better understanding of the basic wear or corrosion mechanisms will lead to an expansion in the applicability of the IBP technologies. Also more needs to be done to encourage other DoD components and DND participation and support in R&D IBP activities.

## **8.4 Sponsor Education Activities**

NATIBO should continue to support activities such as technical workshops, forums, and conferences designed to educate and inform a

wide audience about the benefits, successes, and ongoing R&D and production demonstration efforts related to the IBP technologies. This will assist the IBP technologies in gaining wider commercial and defense acceptance, thereby increasing the potential for dual-use.

At the time of the publication of this report, one such NATIBO-sponsored workshop has already occurred in May 1996 at CCAD. In addition, the U.S. Army and Navy have sponsored four workshops at NDCEE in Johnstown, PA related to environmentally safe alternatives to cadmium and chromium electroplating. The NDCEE workshops have proven to be successful and informative, and have had the effect of focusing both government and industry efforts on these environmental problems.

#### **8.5 Organize a Multilateral, Multiservice IBP Technology Working Group With DoD and DND Co-Chairs**

The IBP technology community is already characterized by very good communications among the researchers and the service providers. There is also a fair amount of joint government activities. The installation and operation of a nitrogen implanter at CCAD, installation of a new, large implanter at NDCEE, the cadmium and chromium electroplating workshops at NDCEE, and DOE technology transfer activities are examples of these joint activities. NATIBO can further assist these efforts by helping to organize a working group consisting of government, industry and academia researchers

and service providers from around the world. The objective will be to collect and disseminate both market and technical related information regarding IBP technologies, and to coordinate the education activities developed in the previous recommendation.

#### **8.6 Collaborate with a Professional or Technical Organization or Both to Explore Possible Commercial IBP Technology Standard Development**

Initially, NATIBO could contact an organization such as the American Society of Testing Methodologies (ASTM) or the American Society of Materials (ASM) to ascertain the possible development of an IBP commercial standard.

Assuming a positive response, NATIBO could then work jointly with DoD and DND components and the associations to develop such a standard. The methodology could include the development of an implementation strategy and a common test protocol to validate IBP technologies against the existing metal finishing techniques.

#### **8.7 Develop an Outreach Program to Specifically Educate and Inform Small Businesses**

NATIBO, in coordination with DoD's and DND's Small Business Programs, could sponsor IBP technology workshops for small business firms providing electroplating services. The objective would be to educate small businesses

on the benefits of IBP technologies, and assist them expand their current business base thereby maintaining their competitive posture and remaining viable sources of metal finishing services to North American commercial and defense industrial bases.

**8.8 Establish Memoranda of Understanding (MoUs) with Foreign Countries**

NATIBO could establish MoUs with foreign countries such as those identified in Section 3.4 of this report with the intent of fostering the joint evolution and acceptance of IBP technology.

**8.9 Collect and Validate Cost Data**

NATIBO could establish a program to collect and extensively validate the capital, operating, and maintenance costs associated with the use of IBP technologies. The data will serve to validate potential cost savings associated with the adoption of IBP technologies. This activity could be initiated at one of the depots or logistic centers that make up the DoD and DND Sustainment Communities

In addition, NATIBO could explore the applicability of Activity Based Accounting practices to better understand the costs associated with IBP technologies. NATIBO could contact one of the North American "Big Seven" accounting firms to assist in this analysis.

## Appendix A Acronyms

AESF	American Electroplaters and Surface Finishers Society
Al	Aluminum
ALC	Air Logistics Center
AMMTRA	Advanced Material Processing and Machining Technology Research Association
ARDEC	U.S. Army Armaments Research Development and Engineering Center
ARL	U.S. Army Research Laboratory
ARPA	Advanced Research Projects Agency
AVIS	Advanced Vacuum-Arc Ion Source
AVSCOM	U.S. Army Aviation Systems Command
B	Boron
Be	Beryllium
BIRL	Basic Industrial Research Laboratory (Northwestern University)
C	Carbon
Ca	Cadmium
Ce	Cerium
CAAA	Clean Air Act Amendments of 1990
CCAD	Corpus Christi Army Depot
CFC	Clorofluorocarbon
Co	Cobalt
Cr	Chromium
CRADA	Cooperative Research and Development Agreement
CTC	Concurrent Technologies Corporation
Cu	Copper
CVD	Chemical Vapor Deposition
CWA	Clean Water Act
DII	Direct Ion Implantation
DLC	Diamond-Like Carbon
DND	Canadian Department of National Defence
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
ECR	Electron Cyclotron Resonance
EM	Electro-Magnetic
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
FDA	Food and Drug Administration
Fe	Iron
GM	General Motors
H-I	Hyper Ion
HHFF	High Heat Flux Facility
HPTF	High Power Test Facility
HRL	Hughes Research Laboratory
HVOF	High Velocity Oxygen Fuel

IAZ	Implantation-Affected Zone
IBAD	Ion Beam Assisted Deposition
IBIS	Inner Bore Ion Source
IBP	Ion Beam Processing
INRS	Institut National de la Recherche Scientifique
ISC	Implant Sciences Corporation
IVD-Al	Ion Vapor Deposited Aluminum
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
mA	milliampere
MAII	Mass Analyzed Ion Implantation
MANTECH	Manufacturing Technology
MeV	Million Electron-Volts
MEVVA	Metal Vapor Vacuum Arc
Mg	Magnesium
MII	Metal Ion Implantation
MIP	Multiple Ion Source Production Implantation System
Mo	Molybdenum
MP&M	Metal Products and Machinery
MPIID	Metal Plasma Immersion Ion Implantation and Deposition
NAMF	National Association of Metal Finishers
NASA	National Aeronautics and Space Administration
NATIBO	North American Technology and Industrial Base Organization
Nb	Niobium
NDCEE	National Defense Center for Environmental Excellence
Ni	Nickel
NIH	National Institutes of Health
NII	Nitrogen Ion Implantation
NRL	Naval Research Laboratory
NSF	National Science Foundation
O	Oxygen
ODC	Ozone Depleting Chemical
OEM	Original Equipment Manufacturer
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Health and Safety Administration
Pd	Palladium
PEL	Permissible Exposure Limit
PMD	Plasma Material Deposition
PSII	Plasma Source Ion Implantation
Pt	Platinum
PVD	Physical Vapor Deposition
R&D	Research and Development
RAMP	Regionally Advanced Manufacturing Program
RAS	Russian Academy of Sciences
RCRA	Resource Conservation and Recovery Act
Re	Rhenium
RF	Radio Frequency
RFQ	Radio Frequency Quadrupole

SBIR	Small Business Innovative Research
SwRI	Southwest Research Institute
Ta	Tantalum
Th	Thorium
Ti	Titanium
UK	United Kingdom
USARO	U.S. Army Research Office
UW	University of Wisconsin
VOC	Volatile Organic Compound
W	Tungsten
Y	Yttrium
Zn	Zinc
Zr	Zirconium

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
1	Abbott, James S.	Hardcoat Anodizing: Low-Cost Coating for Aluminum	Advanced Materials & Processes	Sep-94
2	Advanced Refractory Technologies, Inc.	Diamond-Like Nanocomposite Protective Coatings for the Exterior Surface of Weapon Components (SBIR Summary)	US Marine Corps (Mr. Bryan Prosser)	Sep-95
3	Agarwal, D.C., and W. Herda	Nickel-Based Alloys Combat Corrosion	Advanced Materials & Processes	Jun-95
4	Ahmed, N.A.G., and K. Watkins	Ion assisted deposition for surface engineering	Finishing	Jun-91
5	Alexander, Ralph	Low temperature process reduces wear and galling without dimensional change	The Fabricator (Supplied by Implant Sciences Corp.)	Apr-92
6	Alonso, F., et.al.	Effects of implantation treatments on micromechanical properties of M2 steel	Nuclear Instruments and Methods, B80/81 (1993) 254-257	Jan-95
7	Altmayer, Frank	Metal Finishing in the Philippines	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
8	Anders, Andre, et.al.	Metal plasma immersion ion implantation and deposition using vacuum arc plasma sources	Nuclear Instruments and Methods, B80/81 (1993) 225-228	
9	Andoh, Yasunori, et.al.	Wear resistance of boron nitride coated steel	Encyclopedia of Chemical Technology, Third Edition, Volume 15, John Wiley & Sons	
10	Antonsen, D.H.	Nickel Compounds	Nuclear Instruments and Methods, B80/81 (1993) 1384-1387	
11	Arnault, J.C., et.al.	First stages study of high energy ion beam assisted deposition	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	
12	Arunachalam, V.S., and R. Sundaresan	Powder Metallurgy	Scripta METALLURGICA et MATERIALIA, Vol. 27 (1992) 1639-1643	1991
13	Aus, M.J., et.al.	Magnetic Properties of Bulk Nanocrystalline Nickel		
14	Berkowitz, Joan B., and Newton H. Emerson	Sections from the book Plating Methods: A Survey, NASA SP-5114		
15	BIRL	Engineering Hard Coating Performance: Unbalanced-Magnetron Sputter Coating Technology	BIRL Progress	Jun-91
16	BIRL	Reducing Wear in Machines (Technology Bulletin)	BIRL	1972
17	Blake, J., et.al.	Generation and transport of contamination in high current implanters	Nuclear Instruments and Methods, B 96 (1995) 56-61	
18	Boley, Forrest I.	Plasmas-Laboratory and Cosmic (Book)	D. Van Nostrand Company, Inc., Princeton, N.J.	1966
19	Bond, P., et.al.	A versatile WIBS 200 kV ion implanter for materials modification	Nuclear Instruments and Methods, B55 (1991) 511-516	
20	Borruco, Marty	Polymethylsiloxane Films	Briefing at NDCEE Workshop on Alternatives to Chromium Electropolating	Oct-94
21	Brady Jr., Robert F., and Richard W. Drisko	Marine Coatings	Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, John Wiley & Sons	Feb-93
22	Brooman, Eric W.	Alternatives to Cadmium Coatings for Electrical/Electronic Applications	Plating and Surface Finishing	

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
23	Brown, David and Graham Hubler	Incorporation of Ambient Oxygen During Silicon Deposition and the Effects of Argon Ion Bombardment	Materials Research Society Symposium Proceedings, Vol. 201	1991
24	Brown, I.G., et al.	A broad-beam, high-current metal-ion implantation facility	Nuclear Instruments and Methods, B56 (1991) 508-510 Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
25	Brown, I.G., et al.	Metal ion implantation: Conventional versus immersion	Finishing	Sep-90
26	Brown, Lawrie	Rolling out the barrel	Metal Finishing	Feb-95
27	Budman, Edward	Alkaline Noncyanide Zinc Plating	Encyclopedia of Chemical Technology, Third Edition, Volume 20, John Wiley & Sons	
28	Bunshah, Rointan F., and Donald M. Mattox	Refractory Coatings	Physics Today	
29	Bunshah, Rointan F., and Donald M. Mattox	Applications of metallurgical coatings	Encyclopedia of Semiconductor Technology, Encyclopedia Reprint Series, John Wiley & Sons	
30	Butler, James W.	Ion Implantation	Cadmium Council	May-80
31	Cadmium Association/Cadmium Council	Cadmium production, properties and uses		
32	Cametoid Limited	Cametoid Limited (Fact Sheet)		
33	Carr, D.S.	Cadmium and Cadmium Alloys	Encyclopedia of Chemical Technology, Fourth Edition, Volume 4, John Wiley & Sons	
34	Celler Jr., M.F., P.A. Kohl, and S.A. Bidstrup	Plasma-enhanced chemical vapor deposition of silicon dioxide deposited at low temperatures	Journal of the Electrochemical Society, Vol. 142, No. 6, June 1995, 2067-2071	
35	Chen, A., J. Firmiss, and J.R. Conrad	Dose analysis of nitrogen plasma source ion implantation treatment of titanium alloys	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
36	Chrisey, Douglas B., et al.	Pulsed-Laser Deposition of Ceramic Thin Films	1995 NRL Review (Reprint)	1995
37	Chrysler Corporation	Chromium Containing Corrosion Resistant Coating - Ferrous Metals (Engineering Process Standard)	Chrysler Corp. (Provided by Mr. Ralph White)	Oct-94
38	Chrysler Corporation	Conductive Plated Coatings for Electrical Connectors and Corrosion Protection (Engineering Process Standard)	Chrysler Corp. (Provided by Mr. Ralph White)	Jan-95
39	Chrysler Corporation	Replacement of Cadmium Finishes	Chrysler Corp. (Provided by Mr. Ralph White)	Aug-95
40	Chrysler Corporation	Zinc Alloy Electrodeposited Coatings (Engineering Process Standard)	Chrysler Corp. (Provided by Mr. Ralph White)	May-95
41	Coeling, K.J.	Coating Processes (Spray)	Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, John Wiley & Sons	
42	Collins, G.A., and J. Tendys	Measurements of potentials and sheath formation in plasma immersion ion implantation	J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994, 875-879	
43	Corbitt, Robert A.	Heavy Metals Removal	Pages 6, 170-6, 172 of the Standard Handbook of Environmental Engineering, McGraw-Hill Publishing Company	
44	Corbitt, Robert A.	Liquid Waste Treatment	Pages 9, 19-9, 28 of the Standard Handbook of Environmental Engineering, McGraw-Hill Publishing Company	
45	Corbitt, Robert A.	Wet Scrubbers	Pages 4, 26-4, 35 of the Standard Handbook of Environmental Engineering, McGraw-Hill Publishing Company	

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
46	Coumo, Jerome J., et.al. (editors)	Handbook of Ion Beam Processing Technology (Book)	Noyes Publications	1989
47	Crook, Paul	Cobalt-base alloys resist wear, corrosion, and heat	Advanced Materials & Processes Encyclopedia of Chemical Technology, Fourth Edition, Volume 12, John Wiley & Sons	Apr-94
48	Crooks, Ronald	Hardness	National Center for Manufacturing Sciences/National Association of Metal Finishers	1994
49	Cushnie Jr., George	Pollution Prevention and Control Technology for Plating Operations (Book and Database)	Advanced Materials & Processes	Sep-94
50	Danko, James C., C.D. Lundin, and E.E. Nolting	High-energy electron beam technology	Briefing at NDCEE Workshop on Alternatives to Chromium Electropolating	Oct-94
51	Davidson, Tamara	ENLOY Chromium Alternatives		
52	Dearnaley, G.	Techniques and Equipment for Implantation into Metals	Ion Implantation: Equipment and Techniques, Springer-Verlag	1983
53	Dearnaley, Geoffrey	Altering Material Surfaces to Prolong Service Life	Technology Today (Provided by Geoff Dearnaley)	Mar-94
54	Deb, Diptan, J. Siambis, and R. Symons	Plasma ion implantation technology for broad industrial application	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
55	Dipsol Gumm Ventures	Introducing ZINIC The Zinc Plating Breakthrough (Fact Sheet)	Dipsol Gumm display at NDCEE Workshop on Alternatives to Cadmium Electropolating, May 1995	
56	dos Santos, C.A., and I.J.R Baumvol	Nitriding of Steels: Conventional Processes and Ion Implantation	Ion Implantation: Equipment and Techniques, Springer-Verlag	1983
57	Downey, Daniel F., and G.C. Angel	Metals contamination in high and medium current implanters	Nuclear Instruments and Methods, B96 (1995) 68-74	
58	Dresselhaus, M.S., and R. Kalish	Ion Implantation	Ion Implantation in Diamond, Graphite, and Related Materials; Springer-Verlag	
59	El-Sherik, et.al.	Deviations from Hall-Patch Behaviour in As-Prepared Nanocrystalline Nickel	Scripta METALLURGICA et Materialia, Vol. 27 (1992), 1185-1188	
60	Elves, Robert	Chromium Toxicology	Briefing at NDCEE Workshop on Alternatives to Chromium Electropolating	Oct-94
61	Ensinger, W., A. Schoer, and G.K. Wolf	A comparison of IBAD films for wear and corrosion protection with other PVD coatings	Nuclear Instruments and Methods, B80/81 (1993) 445-454	
62	Ensinger, W., and B. Rauschenbach	Microstructural investigations on titanium nitride films formed by medium energy ion beam assisted deposition	Nuclear Instruments and Methods, B80/81 (1993) 1409-1414	
63	Ensinger, W., et.al.	Ion beam assisted with a dioplasmatron	Review of Scientific Instruments, Vol. 63, No. 5	May-92
64	Environment Canada	Canadian Sediment Quality Guidelines for Cadmium	DND Canada	Dec-94
65	Environment Canada	Canadian Soil Quality Criteria for Contaminated Sites. Ecological Effects: Cadmium (Draft)	DND Canada	Sep-94
66	Environment Canada	Guidelines for the Protection of Freshwater Aquatic Life	DND Canada	
67	Environment Canada	Inorganic Parameters	DND Canada	
68	Environment Canada	Interim Sediment Quality Assessment Values	DND Canada	Sep-94

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
69	Environment Canada	Overview of Guidelines for Canadian Drinking Water Quality 1978	DND Canada	
70	Environment Canada	Overview of the Canadian Surface Finishing Industry	DND Canada	Dec-87
71	Faehi, Ricky, Barbara De Volder and Blake Wood	Application of particle-in-cell simulation to plasma source ion implantation	J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994, 884-888	
72	Follstaedt, David M.	Ion Implantation and Ion Beam Mixing	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	1991
73	Franklyn, C.B., and G. Nothnagel	Nitrogen profiles of high dose, high temperature plasma source ion implantation treated austenitic stainless steel	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
74	Friborg, Lars	Overview of the Health Risks of Cadmium	Introductory Chapter to Cadmium and Health: A Toxicological and Epidemiological Appraisal, Volume I: Exposure, Dose, and Metabolism, CRC Press	
75	Gaughoffer, Johannes, and Vera Bianchi	Chromium	Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance, Edited by Ernest Merian, VCH Publishers, pp. 853-878	
76	Gibbons, James F.	Ion Implantation	Handbook of Semiconductors, Volume 3: Materials, Properties and Preparation, Neth-Holland Publishing Company	1980
77	Glawisching, Hans	Ion Implantation System Concepts	Ion Implantation Techniques, Springer-Verlag	1982
78	Gooden, Capt. William	Development of Spray Casting	Briefing at NDCEE Workshop on Alternatives to Chromium Electroplating	Oct-94
79	Greer, A. Lindsay, and Robert E. Somekh	Metallic Multilayers	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	1991
80	Grobin, Allen W.	Hydrogen Embrittlement Revisited: Part I	Plating and Surface Finishing	Jul-95
81	Grobin, Allen W.	Hydrogen Embrittlement Standards	Plating and Surface Finishing	Feb-95
82	Gruber, William	Deactivation of Inorganic Wastes	Hazardous Materials Management	Oct-93
83	Gunzel, R., et.al.	Plasma source ion implantation of oxygen and nitrogen in aluminum	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
84	Guzman, L., et.al.	Ion implantation and ion beam assisted deposition onto cemented tungsten carbide and sialon	Nuclear Instruments and Methods, B80/81 (1993) 1097-1100	
85	Hamilton, Shirley	"Ioning" out a short life for tooling	Finishing	Oct-91
86	Hanley, P.R.	Physical Limitations of Ion Implantation Equipment	Ion Implantation: Equipment and Techniques, Springer-Verlag	1983
87	Harber, Philip	Biological Monitoring: A Useful Tool in Metal Finishing	Plating and Surface Finishing	Jan-95
88	Harris, M.	Advances in the EXTRION 1000 and XP Series high-current ion implantation systems	Nuclear Instruments and Methods, B55 (1991) 428-433	
89	Harten, Teresa	Alternatives to Hexavalent Chromium in Plating and Metal Finishing	Briefing at NDCEE Workshop on Alternatives to Chromium Electroplating	Oct-94

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
90	Hartley, N.E.W., et.al.	Friction and Wear of Ion Implanted Metals	Applications of Ion Beams to Metals, Plenum Press	1973
91	Heide, N. and J.W. Schulze	Corrosion stability of TiN prepared by ion implantation and PVD	Nuclear Instruments and Methods, B80/81 (1993) 467-471	
92	Heiron, Norman	Cadmium Compounds	Encyclopedia of Chemical Technology, Fourth Edition, Volume 4, John Wiley & Sons	
93	Hirakimoto, Akira, et.al.	The MeV ion implantation system "RFQ-1000" and its applications	Nuclear Instruments and Methods, B55 (1991) 493-501	
94	Holmes, A.J.T., and G. Proudfoot	Negative-ion sources for ion implantation	Nuclear Instruments and Methods, B55 (1991) 323-327	
95	Horelick, Philip D.	Stop Cadmium Plating? Not with Electrochemical Recovery	Plating and Surface Finishing (Provided by the Cadmium Council)	Nov-92
96	Homer, Jack	Electroplating	Encyclopedia of Chemical Technology, Fourth Edition, Volume 9, John Wiley & Sons	
97	Hubler, G.K.	Fundamentals of Ion-Beam-Assisted Deposition: Technique and Film Properties	Materials Science and Engineering, A115, (1989) 181-192	
98	Hubler, G.K.	Surface Treatment with Ion Beam Assisted Deposition	Critical Reviews in Surface Chemistry, 2(3):169-198	1993
99	Hubler, G.K., and F.A. Smidt	Application of Ion Implantation to Wear Protection of Materials	Nuclear Instruments and Methods in Physics Research, B78 (1985) 151-157	
100	Hubler, G.K., E.P. Donovan and C.R. Gossett	Ion beam assisted deposition of hydrogenated amorphous silicon nitride	Nuclear Instruments and Methods, B 91 (1994) 540-544	
101	Hubler, G.K., et.al.	Application of Ion Implantation for the Improvement of Localized Corrosion Resistance of M50 Steel Bearings (NRL Memorandum Report 4481)	NRL (Provided by Dr. Graham Hubler)	Mar-81
102	Hubler, G.K., et.al.	Electrochemical Behavior of an Amorphous Fe-Ti-C Surface in Titanium-Implanted Steel	Ion Implantation Into Metals, Edited by V. Ashworth, Pergamon Press, Oxford and New York	1982
103	Hubler, G.K., et.al.	Fabrication of low-Z X-ray mirrors by ion beam assisted deposition	Nuclear Instruments and Methods in Physics Research, B59/60 (1991) 268-271	
104	Hubler, G.K., et.al.	Fundamentals of ion-beam-assisted deposition II Absolute calibration of ion and evaporation fluxes	J. Vac. Sci. Technol. A 8 (2), Mar/Apr 1990, 831-839	
105	Hubler, G.K., et.al.	Ion Beam Assisted Deposition of Titanium Nitride	Materials Research Society Symposium Proceedings, Vol. 128	1989
106	Hubler, G.K., et.al.	Physical Aspects of Ion Beam Assisted Deposition	Nuclear Instruments and Methods in Physics Research, B46 (1990) 384-391	
107	Hubler, Graham K.	Microstructural Evolution During Ion Beam Assisted Deposition	Materials Research Society Symposium A Proceedings	Fall 1994
108	Hubler, Graham K. and James K. Hirvonen	Ion-Beam-Assisted Deposition	NRL (Provided by Dr. Graham Hubler)	1994
109	Hubler, R., and G.K. Wolf	Ion beam mixing of Al-AlN multilayers for tribological and corrosion protection	Nuclear Instruments and Methods, B80/81 (1993) 1415-1418	
110	Husky	Closure Molds	Husky Injection Molding	May-94
111	Husky	Hot Runner Systems	Husky Injection Molding	Sep-93
112	Husky	ITS Integrated Two-Stage Stretch Blow Molding System	Husky Injection Molding	Oct-93
113	Husky	Moduline 180 to 825 Ton Machines	Husky Injection Molding	May-94

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
114	Husky	Profile 1994	Husky Injection Molding	Oct-94
115	Implant Sciences Corporation	Implant Sciences Corporation (Fact Sheet)	Implant Sciences Corporation	Aug 95
116	Implant Sciences Corporation	Ion Implantation...improves tool life 400%	Implant Sciences Corporation	Aug 95
117	Inami, H., et.al.	Development of a high-current and high-energy metal ion beam system	Nuclear Instruments and Methods, B55 (1991) 370-373	
118	Ishikawa, Junzo, et.al.	Negative-ion implantation technique	Nuclear Instruments and Methods, B96 (1995) 7-12	
119	ISM Technologies	Filtered Cathodic Arc Source (Fact Sheet)		
120	ISM Technologies	Metal Ion Implantation: Process Comparisons (Fact Sheet)		
121	ISM Technologies	MEVVA: Metal Ion Implantation Systems (Fact Sheet)		
122	Jeffers, T.H., P.G. Bennett and R.R. Corwin	Biosorption of Metal Contaminants Using Immobilized Biomass-Field Studies	U.S. Dept. of Interior, Bureau of Mines Encyclopedia of Chemical Technology, Third Edition, Volume 20, John Wiley & Sons	1993
123	Johnson Jr., James S.	Reverse Osmosis	U.S. Dept. of the Interior, Bureau of Mines: Also Resources, Conservation and Recycling, 9 (1993) 1-30	
124	Jolly, James H.	Materials flow of zinc in the United States 1850-1990		1993
125	Kamenitsa, Dennis E., and R.D. Rathmell	Beam energy purity in the Eaton NV-8200P ion implanter	Nuclear Instruments and Methods, B96 (1995) 13-17	
126	Katz, Sidney A., and Harry Salem	The Biological and Environmental Chemistry of Chromium (Book)	VCH Publishers	1994
127	Kawai, T., et.al.	The Nissan PR-80A high current ion implantation system	Nuclear Instruments and Methods, B55 (1991) 443-447	
128	Kelley, Maryellen R., and Todd A. Watkins	In From The Cold: Prospects for Conversion of the Defense Industrial Base	Science, Vol. 268, 28 April 1995	
129	Kenny, M.J., et.al	A comparison of plasma immersion ion implantation with conventional ion implantation	Nuclear Instruments and Methods, B80/81 (1993) 262-266	
130	Kiuchi, Masato	Advantages of dynamic ion beam mixing	Nuclear Instruments and Methods, B80/81 (1993) 1343-1348	
131	Kollitsch, A., E. Hentschel, and E. Richter	Depth profiles of C, N, and O on carbon coated steel surfaces made by BAD	Nuclear Instruments and Methods, B80/81 (1993) 258-261	
132	Komarov, Fadei	Ion Beam Modification of Metals	Pages 198-215 of the book Ion Beam Modification of Metals, Gordon and Breach Science Publishers, translated from the Russian by Paul Curtis	
133	Korenev, S.	Pulsed ion sources for surface modification of materials	Nuclear Instruments and Methods, B80/81 (1993) 242-245	
134	Kraft, Gerald G.	The Future of Cadmium Electroplating	Metal Finishing Encyclopedia of Semiconductor Technology, Encyclopedia Reprint Series, John Wiley & Sons	Aug 90
135	Kruilk, Gerald A.	Electroless Plating	Encyclopedia of Chemical Technology, Fourth Edition, Volume 9, John Wiley & Sons	
136	Kruilk, Gerald A.	Electroless Plating	Encyclopedia of Chemical Technology, Third Edition, Volume 15, John Wiley & Sons	
137	Krutenat, R.C.	Metallic Coatings (Survey)	U.S. Dept. of the Interior, Bureau of Mines Nickel, 1993 Annual Report	Mar 95
138	Kuck, Peter H.			

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
139	Lamancusa, James P.	Strategies at a Decorative Chromium Electropolating Facility: On-line vs. Off-line Recycling	Plating and Surface Finishing Regulatory Chemicals of Health and Environmental Concern, Van Nostrand Reinhold Company	Apr-95
140	Lederer, William H.	Chemical Compound Descriptions (Cadmium compounds, Chromium compounds, et.al.) Environmental Engineering Glossary and Acronym List	Environmental Engineering Dictionary, Second Edition, Government Institutes, Inc.	
141	Lee, C.C.		Encyclopedia of Semiconductor Technology, Encyclopedia Reprint Series, John Wiley & Sons	
142	Lee, Stuart M.	Film Deposition Techniques	Briefing at NDCEE Workshop on Alternatives to Chromium Electropolating	Oct-94
143	Legg, Keith	BIRL-ARPA Program		
144	Legg, Keith O.	Dry Coating Alternatives to Hard Chrome: Are They Commercially Viable	BIRL	
145	Legg, Keith O.	Les Procedes "Secs" de Substitution du Chrome Dur: Sont-ils Commercialment Viables? (Briefing in English)	BIRL	1994
146	Lindsay, James H.	Special Conference Comes to Grips with Hexavalent Chromium	Plating and Surface Finishing	Feb-95
147	Llewellyn, Thomas O.	Cadmium (Materials Flow) (IC 9380)	U.S. Dept. of Interior, Bureau of Mines Encyclopedia of Chemical Technology, Third Edition, Volume 24, John Wiley & Sons	1994
148	Lloyd, Thomas B.	Zinc Compounds	Encyclopedia of Chemical Technology, Third Edition, Volume 24, John Wiley & Sons	
149	Lloyd, Thomas B., and W. Showak	Zinc and Zinc Alloys	Plating and Surface Finishing	
150	Loncea, Michel	Dacrotizing-an effective protection against corrosion		Sep-90
151	Long, N.J.T.	Substitution of hazardous substances in the finishing industries		Jan-91
152	Mack, M.E., et.al	Particle generation in ion implanters	Nuclear Instruments and Methods, B96 (1995) 80-86 Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
153	Malik, Shamim M., et.al.	Overview of plasma source ion implantation research at University of Wisconsin-Madison		
154	Manty, Brian, and Melissa Weis	Characterization of Current Electropolating Processes		
155	Marce, Roger E.	ITT Cannon Connects with Cadmium	Cadmium Council	
156	Matossian, Jesse N.	Plasma ion implantation at Hughes Research Laboratories	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
157	Mattox, Donald M.	Hard Coatings by PVD	Plating and Surface Finishing	Jan-95
158	Mattox, Donald M.	Plasma Chemistry & PVD Processes	Plating and Surface Finishing	Jun-95
159	Mattox, Donald M.	PVD Processes: Characterization of Surface Morphology	Plating and Surface Finishing	Mar-95
160	Mattox, Donald M.	Substrates for Tribological Coatings	Plating and Surface Finishing	Apr-95
161	McCafferty, E., et.al.	Effect of Laser Processing and Ion Implantation on Aqueous Corrosion Behavior	Proceedings of the October 1981 Metallurgical Society of AIMI Symposium on Corrosion of Metals Processed by Directed Energy Beams	Oct-81

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
162	McCafferty, E., et.al.	Naval Research Laboratory Surface Modification Program: Ion Beam and Laser Processing of Metal Surfaces for Improved Corrosion Resistance	Materials Science and Engineering, 86 (1987) 1-17	
163	McCafferty, E., G.K. Hubler and J.K. Hirvonen	Corrosion Control By Ion Implantation	Proceedings of the 1978 Tri-Service Conference on Corrosion, M. Levy and J. Brown, eds., p. 435	1979
164	McCafferty, E., P.M. Natishan and G.K. Hubler	Ion beam processing of metal surfaces for improved corrosion resistance	Nuclear Instruments and Methods in Physics Research, B56/57 (1991) 639-643	
165	McCafferty, E., P.M. Natishan and G.K. Hubler	Ion Beam Surface Modification of Aluminum Alloys	Corrosion Science, Vol. 35, Nos. 1-4, pp. 239-246	1993
166	McCafferty, E., P.M. Natishan and G.K. Hubler	The Anodic Behavior of Ion Beam Mixed Surface Alloys	Corrosion Science, Vol. 30, No. 2/3, pp. 209-221	1990
167	McComas, Charles	Nickel Boron: An Alternative to Chromium Plate	Briefing at NDCEE Workshop on Alternatives to Chromium Electroplating	Oct-94
168	McIntyre, E., et.al.	Initial performance results from the NV1002 high energy Ion Implanter	Nuclear Instruments and Methods, B55 (1991) 473-477	
169	Metal Coatings International	Dacroizing and Dacrosealing (Booklet)		
170	Metal Finishing Suppliers Association	Zinc and Cadmium Coatings	NRL (Provided by Dr. Graham Hubler)	1987
171	Mihara, Y., et.al.	Parallel beam ion implanter: IPX-7000	Nuclear Instruments and Methods, B55 (1991) 417-422	
172	Moffatt, S.	Ion implantation from the past and into the future	Nuclear Instruments and Methods, B96 (1995) 1-6	
173	Moran, Patrick J., and Paul M. Natishan	Corrosion and Corrosion Control	Encyclopedia of Chemical Technology, Fourth Edition, Volume 7, John Wiley & Sons	
174	Mordike, Barry L.	Surface Modification by Lasers	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	1991
175	Morrow, Hugh	Cadmium Coatings Have a Future	International Cadmium Association	May-95
176	Morrow, Hugh	Cadmium Electropolating	International Cadmium Association	
177	Morrow, Hugh	The Environmental and Engineering Advantages of Cadmium Coatings. (Briefing)	International Cadmium Association	Oct-95
178	Morrow, Hugh	The Environmental and Engineering Advantages of Cadmium Coatings (Paper)	International Cadmium Association	Oct-95
179	Morrow, Hugh	Update on Worldwide Cadmium Recycling (Briefing)	International Cadmium Association	May-95
180	Morrow, Hugh	Update on Worldwide Cadmium Recycling (Paper)	International Cadmium Association	May-95
181	Mosser, Mark	Metallic-Ceramic Coatings as Replacements for Cadmium Plating	Society of Automotive Engineers Technical Paper Series, No. 900968	Apr-90
182	Murphy, Michael	Focus on Chromium	Metal Finishing	Aug-95
183	N & W Metal Finishing	Approved Finishing List	N & W Metal Finishing display at NDCEE Workshop on Alternatives to Cadmium Electropolating, May 1995	
184	N & W Metal Finishing, Inc.	N & W Metal Finishing, Inc. (Booklet)	N & W Metal Finishing display at NDCEE Workshop on Alternatives to Cadmium Electropolating, May 1995	
185	Nagai, N., et.al.	The Nissan NH-20SP medium current ion implanter	Nuclear Instruments and Methods, B55 (1991) 393-397	

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
186	Nagasaki, Hiroshi, et.al.	The properties of titanium nitride prepared by dynamic ion mixing	Nuclear Instruments and Methods, B80/81 (1993) 1380-1383	Nov-94
187	Nanometals Corporation	Nanometals Fact Sheet	Nanometals Corp.	
188	Nasser-Ghodsi, M., et.al.	A high-current ion implanter system	Nuclear Instruments and Methods, B55 (1991) 398-407	
189	Natishan, P.M., E. McCafferty and G.K. Hubler	Surface Charge Considerations in the Pitting of Ion-Implanted Aluminum	Journal of the Electrochemical Society, Vol. 135, No. 2, February 1988, 321-327	
190	Natishan, P.M., E. McCafferty and G.K. Hubler	The Corrosion Behavior of Mo-Al, Cr-Al and Cr-Mo-Al Surface Alloys Produced by Ion Beam Mixing and Ion Implantation	Corrosion Science, Vol. 32, No.7, pp. 721-731	1991
191	Natishan, P.M., E. McCafferty and G.K. Hubler	The Effect of pH of Zero Charge on the Pitting Potential	Journal of the Electrochemical Society, Vol. 133, No. 5, May 1986, 1061-1062	
192	Natishan, P.M., E. McCafferty and G.K. Hubler	The pitting corrosion behavior of aluminum ion implanted with tantalum	Nuclear Instruments and Methods in Physics Research, B59/60 (1991) 841-844	
193	Natsuaki, Nobuyoshi, et.al.	ULSI-process demands of contamination control on ion implantation	Nuclear Instruments and Methods in Physics Research B, B96 (1995) 62-67	
194	NDCEE	Advanced Techniques for Replacing Chromium: An Information Exchange		Oct-94
195	NDCEE	Advanced Techniques for Replacing Chromium: An Information Exchange. Agenda and Abstracts		Oct-94
196	NDCEE	An Overview of Inorganic Coating Processes		Oct-94
197	NDCEE	Assessment of Alternatives to Existing Chromate Conversion Coating for Aluminum Alloys on Large Aircraft		Sep-93
198	NDCEE	Cadmium Alternatives	NDCEE Update, Vol. 1, No. 5	Aug-95
199	NDCEE	Cadmium Alternatives: An Information Exchange. Agenda and Abstracts		May-95
200	NDCEE	Cadmium Alternatives: An Information Exchange. Proceedings		Jul-95
201	NDCEE	Capabilities Summary		
202	NDCEE	Characterization of Current Electropolating Processes	From the NDCEE Effr. 1 " Ion Beam Processing for Environmentally Acceptable Coatings"	Aug-94
203	NDCEE	Ion Beam Processing for Environmentally Acceptable Coatings. Selection of Materials/Components	NDCEE	Oct-94
204	NDCEE	Ion Implantation/Ion Beam Assisted Deposition System Specification	From the NDCEE Effr. 1 " Ion Beam Processing for Environmentally Acceptable Coatings"	Jan-95
205	NDCEE	Nickel Electropolating	NDCEE	Oct-93
206	NDCEE	Regulatory Analysis of the Chromium Electropolating Industry and Technical Alternatives to Hexavalent Chromium Electropolating	From the NDCEE Effr. 1 " Ion Beam Processing for Environmentally Acceptable Coatings"	Jan-95
207	NDCEE	Selection of Materials/Coatings	From the NDCEE Effr. 1 " Ion Beam Processing for Environmentally Acceptable Coatings"	Oct-94
208	NDCEE	Task Descriptions	From the NDCEE Effr. 1 " Ion Beam Processing for Environmentally Acceptable Coatings"	Spring 1995

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
209	NDCEE	Technical Alternatives to Cadmium Electropolating Waterjet Installed at Corpus Christi Army Depot	NDCEE Update, Vol. 1, No. 4	Sep-94
210	NDCEE	Determination of Tivalent Chromium in Chromium Plating Electrolytes	Metal Finishing	Apr-95
211	Nikolova, S., T. Dobrev, and M. Monev	Hydrogen Permeation Behavior in Polycrystalline Nickel Implanted with Helium, Argon, Nickel, Yttrium and Platinum	Materials Science and Engineering, 90 (1987) 243-251	May-95
212	Nishimura, R., R.M. Latanision and G.K. Hubler	Risk Reduction Monograph No. 5: Cadmium (OECD Environment Monograph Series No. 104)	International Cadmium Association	1994
213	Organisation for Economic Co-operation and Development (HQ: Paris)	Chromium Compounds	Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, John Wiley & Sons	
214	Page, Billie J., and Gary W. Loar	Interocrystalline Hydrogen Transport in Nanocrystalline Nickel	Scripta METALLURGICA et MATERIALIA, Vol. 25 (1991) 679-684	
215	Palumbo, G., et.al.	Chromium Life Cycle Study	U.S. Dept. of the Interior, Bureau of Mines Information Circular 9411	
216	Papp, John F.	Industrial Wastewater Treatment	Encyclopedia of Environmental Science and Engineering, Third Edition, Revised and Updated, Volume One, Gordon and Breach Publishers	1994
217	Parker, Clinton E., and Syed R. Qasim	Practical Application of HVOF Thermal Spray Technology for Navy Jet Engine Overhaul & Repair	Plating and Surface Finishing	
218	Parker, Donald S.	Effect of ion implantation on the residual stress, tribological and machining behavior of CVD and PVD TiN coated cemented carbide cutting tool inserts.	Surface and Coatings Technology, 68/69 (1994) 294-300	Jul-95
219	Perry, Anthony J., et.al.	Cyanides	Encyclopedia of Chemical Technology, Fourth Edition, Volume 7, John Wiley & Sons	
220	Pesce, Lawrence D.	Ion implantation metallurgy	Physics Today	Nov-84
221	Picraux, S. Thomas	EXTRON 220 medium-current ion implanter	Nuclear Instruments and Methods, B55 (1991) 423-427	
222	Pippins, Michael W.	A system and performance overview of the	Cadmium Council	
223	Poll, Gerard H.	Reilly Plating: All Automotive	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
224	Reass, William A.	Survey of high-voltage pulse technology suitable for large-scale plasma source ion implantation processes	Advanced Materials & Processes	Dec-94
225	Reeber, R.R., and K. Sridharan	Plasma Source Ion Implantation	Ion-Solid Interactions: Fundamentals and Applications, by M. Nastasi and J.W. Mayer, to be published by Cambridge University Press	
226	Rej, D.J.	Plasma Source Ion Implantation	J. Vac. Sci. Technol. B 12(4), Jul/Aug 1994, 2380-2387	
227	Rej, D.J., and Ralph B. Alexander	Cost estimates for commercial plasma source ion implantation	Materials Research Society Symposium Proceedings, Vol. 316	
228	Rej, D.J., et.al.	First Results from the Los Alamos Plasma Source Ion Implantation Experiment	Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, John Wiley & Sons	1994
229	Richart, Douglas S.	Coating Processes (Powder Technology)		

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
230	Rofaghha, R., et.al.	The Corrosion Behaviour of Nanocrystalline Nickel	Scripta METALLURGICA et Materialia, Vol. 25 (1991) 2867-2872	
231	Roos, Jef R., Jean-Pierre Celis and Marc De Bonté	Electrodeposition of Metals and Alloys Low energy N(15) and N(14) implantation in chromium analysed by NRA and RBS	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	1991
232	Rose, M., et.al.	Improvement in wear characteristics of steel tools by metal ion implantation	Nuclear Instruments and Methods, B80/81 (1993) 459-462	
233	Ruck, D.M., D. Boos, and I.G. Brown	Significance of nitrogen mass transfer mechanism on the nitriding behavior of austenitic stainless steel	Nuclear Instruments and Methods, B80/81 (1993) 233-236	
234	Samandi, M., et.al.	Control Corrosion with New Nickel-Base Alloys	J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994, 935-939	
235	Schade, J.P., R.W. Ross Jr	Plasma Source Ion Implantation of Ammonia into Electropolished Chromium	Advanced Materials & Processes	Jul-94
236	Scheuer, J.T., et.al.	Plasma Source Ion Implantation (PSII) (Briefing)	Los Alamos National Laboratory, submitted to the TMS Annual Meeting, Las Vegas, NV	Feb-95
237	Scheuer, Jay T.	Sematech Dense Pack Coatings: Replacements for Cadmium Plating (Fact Sheet)	Los Alamos National Laboratory	
238	Sernatech International	Sernatech display at NDCEE Workshop on Alternatives to Cadmium Electropolating, May 1995	Sernatech	
239	Shedd, Kim B.	The Materials Flow of Cobalt in the United States Study of surface modification of WC-Co alloy by nitrogen implantation	U.S. Dept. of the Interior, Bureau of Mines Nuclear Instruments and Methods in Physics Research B80/81 (1993) 229-232	1993
240	Shi, W.D., et.al.	Organic Sealants for Anodized Aluminum: A New Method for Corrosion Protection	Briefing at NDCEE Workshop on Alternatives to Chromium Electropolating	
241	Shulman, Garson P., et.al.	Charge neutralization in ion implanters	Nuclear Instruments and Methods in Physics Research B 96 (1995) 22-29	
242	Smatlak, D.L., M.E. Mack and S. Mehta	Surface Modification by Ion Implantation	NRL (Provided by Dr. Graham Hubler)	
243	Smidt, F.A.	The Use of Ion Implantation for Materials Processing. Annual Progress Report for the Period 1 October 1980 - 30 September 1981	NRL Memorandum Report 4821 (Provided by Dr. Graham Hubler)	Oct-86
244	Smidt, F.A.	The Use of Ion Implantation for Materials Processing. Annual Progress Report for the Period 1 October 1981 - 30 September 1982	NRL Memorandum Report 5177 (Provided by Dr. Graham Hubler)	Oct-86
245	Smidt, F.A.	The Use of Ion Implantation for Materials Processing. Annual Progress Report for the Period 1 October 1983 - 30 September 1984	NRL Memorandum Report 5716 (Provided by Dr. Graham Hubler)	Sep-83
246	Smidt, F.A.	The Use of Ion Implantation for Materials Processing. Annual Progress Report for the Period 1 October 1984 - 30 September 1985	NRL Memorandum Report 5898 (Provided by Dr. Graham Hubler)	Mar-86
247	Smidt, F.A.	Use of ion beam assisted deposition to modify the microstructure and properties of thin films	International Materials Reviews, Vol. 35, No. 2, pp. 61-128	Dec-86
248	Smidt, F.A.	Recent advances in ion beam modification of metals	Nuclear Instruments and Methods, B80/81 (1993) 207-216	1990
249	Smidt, F.A., and G.K. Hubler	Preliminary Evaluation of Ion Implantation as a Surface Treatment to Reduce Wear of Tool Bits	Ion Implantation for Materials Processing, Noyes Publications	1983
250	Smidt, F.A., J.K. Hirvonen, and S. Ramalingam			

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
251	Smidt, Fred A.	Ion-beam-assisted Deposition Provides Control over Thin Film Properties	NRL Pub 215-4670 (Provided by Dr. Graham Hubler) Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	May-92
252	Smith, Preston, et.al.	Enhanced pitting corrosion resistance of 304L stainless steel by plasma ion implantation		
253	Spire Corporation	Final Report for: Ion Implantation Manufacturing Technology Program	NRL (Provided by Dr. Graham Hubler)	Jan-87
254	Spire Corporation (Ray Bricault)	Ion Beam Assisted Deposition: An Environmentally Benign Alternative to Wet Chemical Plating	Briefing at NDCEE Workshop on Alternatives to Chromium Electroplating	Oct-94
255	Sprout, W.D., et.al.	Reactive sputtering in the ABS system	Surface and Coatings Technology, 56 (1993) 179-182	
256	Sprout, William D.	Ion-assisted deposition in unbalanced-magnetron sputtering systems	Materials Science and Engineering, A163 (1993) 187-192	
257	Sprout, William D.	Multi-cathode unbalanced magnetron sputtering systems	Surface and Coatings Technology, 49 (1991) 284-289	
258	Sprout, William D.	Multilayer, multicomponent, and multiphase physical vapor phase deposition coatings for enhanced performance	J. Vac. Sci. Technol. B 12(4), Jul/Aug 1994, 1595-1601	
259	Sprout, William D., et.al.	Reactive unbalanced magnetron sputtering of the nitrides of Ti, Zr, Hf, Cr, Mo, Ti-Al, Ti-Zr and Ti-Al-V	Surface and Coatings Technology, 61 (1993) 139-143	
260	Stoeppler, Markus	Cadmium	Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance. Edited by Ernest Merian, VCH Publishers, pp. 803-851	
261	Sugiyama, Kenji, et.al.	Basic characteristics of chromium nitride films by dynamic ion beam mixing	Nuclear Instruments and Methods, B80/81 (1993) 1376-1379	
262	Suryanarayana, C.	Rapid Solidification	Materials Science and Technology: A Comprehensive Treatment, Volume 15, Processing of Metals and Alloys, VCH Publishers	1991
263	Tanabe, N., and M. Iwaki	Effects of Ar ion beam bombardment on the formation of cubic BN in IBED	Nuclear Instruments and Methods, B80/81 (1993) 1349-1355	
264	Tang, Bao Yin	Development of plasma source ion implantation in China	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
265	Tashlykov, I.S., et.al.	Improvement of physical and chemical properties of steel implanted with Cr <sup>+</sup> , Ti <sup>+</sup> , Si <sup>+</sup> ions	Nuclear Instruments and Methods in Physics Research B80/81 (1993) 271-274	
266	Thom, Robert, et.al.	Rolling contact fatigue tests of reactively sputtered nitride coatings of Ti, Zr, Hf, Cr, Mo, Ti-Al, Ti-Zr and Ti-AlV on 440C stainless steel	Surface and Coatings Technology, 62 (1993) 423-427	
267	Thomas, K., M.J. Alport and T.E. Sheridan	Two ion fluid model for plasma source ion implantation	J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994, 901-904	
268	Tien, John K., and T.E. Howson	Nickel and Nickel Alloys	Encyclopedia of Chemical Technology, Third Edition, Volume 15, John Wiley & Sons	
269	Torcad Limited	Torcad Limited (Fact Sheet)		

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
270	Treglio, J.R., and A.J. Perry	Metal Ion Beams for Sputter Cleaning and Deposition Assistance	Society of Vacuum Coaters, 37th Annual Technical Conference Proceedings	1994
271	Treglio, J.R., S. Trujillo, and A.J. Perry	Deposition of TiB2 at low temperature with low residual stress by a vacuum arc plasma source	Surface and Coatings Technology, 61 (1993) 315-319	
272	Treglio, James R., A.J. Perry, and A.F. Tian	Eye on Ions	Cutting Tool Engineering, Volume 47, No. 1	Feb-95
273	Treglio, James R., A.J. Perry, and R.J. Skinner	Ion Beams Replace Chrome Plating	Advanced Materials & Processes	May-95
274	Treglio, James R., A.J. Perry, and R.J. Skinner	The economics of metal ion implantation	Surface and Coatings Technology, 65 (1994) 184-188	
275	Tsukakoshi, Osamu, et.al.	A high-current low-energy multi-ion beam deposition system	Nuclear Instruments and Methods, B55 (1991) 355-358	
276	U.S. Dept. of Defense	Dual Use Technology		Feb-95
277	U.S. Dept. of Labor, OSHA	Occupational Exposure to Cadmium (OSHA 3136)	Cadmium Council	1992
278	U.S. Dept. of Labor, OSHA	OSHA Final Rule: Occupational Exposure to Cadmium	Cadmium Council	Sept-92
279	U.S. Dept. of the Interior, Bureau of Mines	Mineral Commodity Summaries 1991	Bureau of Mines	1991
280	U.S. Dept. of the Interior, Bureau of Mines	Mineral Industry Surveys: Cadmium in 1993	Bureau of Mines	Nov-94
281	U.S. EPA	Common Sense Initiative Update	EPA	Apr-95
282	U.S. EPA	The Common Sense Initiative: A New Generation of Environmental Protection	EPA	Jun-95
283	U.S. EPA	U.S. Environmental Protection Agency Common Sense Initiative Status Report: Metal Finishing Sector	EPA	Jul-95
284	Vachon, D.T., et.al.	Evaluation of Electrochemical Recovery of Cadmium at a Metal Finishing Plant	Plating and Surface Finishing	
285	Vachon, Derek, and Larry Whittle	A Training Course in Pollution Prevention Planning in the Metal Finishing Industry (Course Notes)		May-95
286	Valori, R., D. Popgostev and G.K. Hubler	Ion Implanting Bearing Surfaces for Corrosion Resistance	Transactions of the ASME, Vol. 105	Oct-83
287	Van Vechten, D., et.al.	Fundamentals of ion-beam-assisted deposition I		
288	Vyatkin, A.F., et.al.	Model of process and reproducibility of film composition	J. Vac. Sci. Technol. A 8(2), Mar/Apr 1990, 821-830	
289	Walter, K.C.	Development of ion implantation equipment in the USSR	Nuclear Instruments and Methods, B55 (1991) 386-392	
290	Wang, S., et.al.	Nitrogen plasma source ion implantation of aluminum	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
291	Was, G.S., et.al.	Corrosion Evaluation of Electrodeposited Bulk Nanocrystalline Nickel	Nanometals Corporation (Mr. Donald Wood)	
292	Wastewater Technology Centre	Synthesis and properties of microaluminate structures by ion beam assisted deposition	Nuclear Instruments and Methods, B80/81 (1993) 1356-1361	
293	Wastewater Technology Centre	Site Remediation (Fact Sheet)		
294	Wastewater Technology Centre	Wastewater Technology Centre (Booklet)		
295	Webster, Donald	Wastewater Technology Centre (Brochure)		
		Aluminum-Lithium Alloys. The Next Generation	Advanced Materials & Processes	May-94

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
296	Weis, Melissa	Ion Beam Processing for Environmentally Acceptable Coatings	Briefing at NDCEE Workshop on Alternatives to Chromium Electroplating	Oct-94
297	Westbrook, Jack H.	Chromium and Chromium Alloys	Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, John Wiley & Sons	
298	Wheaton, R.M., and L.J. Lefevre	Ion Exchange	Encyclopedia of Chemical Technology, Third Edition, Volume 13, John Wiley & Sons	
299	White, Ralph W.	Double Teaming the Elimination of Cadmium-Part 1	Fastener Technology International Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	Apr-95
300	Wood, B.P., et.al.	Initial operation of a large-scale plasma source ion implantation experiment		
301	Wood, B.P., et.al.	Initial Operation of a large-scale plasma source ion implantation experiment	J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994, 870-874	
302	Wood, D.E., U. Erib, and R. Rofagha	Nanocrystalline Materials by Electrodeposition-Complementary or Competitive to Thermal Spray Coatings?	Nanometals Corporation (Mr. Donald Wood)	
303	Wood, Donald E.	Letter to Sylvia Jeffrey Re: Nanocrystalline Metals & Alloys by Electrodeposition		Jun-95
304	Wright, D.A., N.Gage and B.A. Wilson	Zinc-Nickel Electroplate As A Replacement for Cadmium on High-Strength Steels	Plating and Surface Finishing	Jul-94
305	Wright, Donald, N. Gage, and P. Bushnell	Verification of the Development of Low Hydrogen Embrittling Zinc-Nickel Electroplate by Slow Strain Rate Testing	Metal Finishing	Apr-95
306	Wurm, Jorg	Chromium plating with platinised titanium anodes	Finishing	May-90
307	Xi, Wang, et.al.	Characteristics of the nitrogen ion implanted intermetallic compound TiAl	Nuclear Instruments and Methods, B80/81 (1993) 250-253	
308	Xia, Lifang, et.al.	Structure and wear behavior of nitrogen-implanted aluminum alloys	Papers from the First International Workshop on Plasma-Based Ion Implantation, J. Vac. Sci. Technol. B 12(2), Mar/Apr 1994	
309	Yao, X.Y., et.al	The pitting corrosion behavior of aluminum ion implanted with titanium	Nuclear Instruments and Methods, B80/81 (1993) 267-270	
310	Zahn, Mark	The Mettle of Metals	Plating and Surface Finishing	
311	Zaki, Nabil	Zinc-Nickel Alloy Plating	Metal Finishing	
312		Cadmium Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.7	Jan-95
313		Chromium Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.16	Jun-89
314		Cobalt Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.11	1968
315		Compounds of Chromium Molybdenum and Tungsten	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.15	1968
316		Conference Announcement and Speaker List: Nano-Particulates 94	Nanometals Corporation (Mr. Donald Wood)	

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
317		Corrosion of Metals	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume III, Section 11.5	1970
318		European Council Directive Restricting Cadmium	Cadmium Council	Jun-91
319		How Crown City Plating Co. Spells Success: Teamwork Through Innovation, Communication & Environmental Leadership	Plating and Surface Finishing	Apr-95
320		Ion Implantation Gets Serious	Modern Applications News	Jan-95
321		Ion Implantation Slashes Tooling Costs	Cutting Tool Engineering, Volume 45, No. 7	Oct-93
322		Ion Implanted Inserts Work Inconel	Modern Applications News	Jun-94
323		Lead Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 13.5	1968
324		Letter from Polymer Research Corp. of America to Harry Lake re: Chemical Grafting	Modern Applications News	Feb-95
325		Literature Available from NiDI	Nickel Development Institute	Apr-95
326		Metal Finishing 62nd Guidebook and Directory Issue	Metal Finishing	1994
327		Metal Implantation System Saves Money	Modern Applications News	Oct-93
328		Metallic Compound Descriptions and their Biological Relevance (Cadmium compounds, Chromium compounds, et.al.)	Metals and Their Compounds in the Environment, VCH Publishers	
329		Nickel Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.12	1968
330		NiDI: Global Connections	Nickel Development Institute	Dec-93
331		Plating Wastes	CRC Handbook of Environmental Control, Volume IV: Wastewater: Treatment and Disposal, CRC Press	
332		Reflecting on the Environment	Finishing	May-90
333		Stablex Canada (Information Sheets)	DND Canada	1994
334		The Surface Treatment of Metals	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume III, Chapter 9	1970
335		Thermal Spray. Technology Update	Advanced Materials & Processes	May-94
336		Tin Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 13.4	1968
337		Various sections related to metals and their compounds in the environment	Metals and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance, Edited by Ernest Merian, VCH Publishers	
338		Zinc Compounds	Chemical Technology: An Encyclopedic Treatment, Barnes & Noble, Volume I, Section 14.6	1968
339				
340				
341				
342				
343				
344				
345				

## Appendix B - Bibliography

ID #	Author	Title	Source	Date
346				
347				

**Appendix C - Points of Contact**

Point of Contact		Company Name	Company Address				Phone Number
Last Name	First Name		Address	City	State/Prov	Zip Code	
Adjourlolo	Alain	Boeing Defense and Space Group	P.O. Box 3999, MS 82-	Seattle	WA	98124-2499	(206) 773-2271
Armini	Tony	Implant Sciences Corp.	107 Audobon Road, #5	Wakefield	MA	01880	(617) 246-0700
Arps	Jim	Southwest Research Institute	6220 Culebra Road	San Antonio	TX	78228	(210) 522-6588
Beat	Thomas	Lawrence Livermore National Laboratory		Livermore	CA		(510) 422-5492
Bernecki	Thomas	BIRL, Northwestern University	1801 Maple Avenue	Evanston	IL	60201	(708) 491-2448
Blake	Julian	Eaton Corporation	108 Cherry Hill Drive	Beverly	MA	01915	(508) 921-9753
Brown	Ian	Lawrence Berkeley National Laboratory	University of California	Berkeley	CA	94720	(510) 486-4174
Class	Walter	Eaton Corporation	108 Cherry Hill Drive	Beverly	MA	01915	(508) 921-9750
Conrad	John	University of Wisconsin	1500 Engineering Dr.	Madison	WI	53706	(608) 263-4789
Constable	Tom	Wastewater Technology Centre	867 Lakeshore Road, P.O. Box 5068	Burlington	Ont.	L7R 4L7	(905) 336-4617
Davis	Harold	Los Alamos National Lab	Physics Division, Mail Stop E526	Los Alamos	NM	87545	(505) 667-8373
Dearnaley	Geoff	Southwest Research Institute	6220 Culebra Road	San Antonio	TX	78228	(210) 522-5579
Degrenier	Edward	Diamond Composite Technology	151 S. Pfingsten Road, Unit D	Deerfield	IL	60015	(708) 498-3710
Deutchman	Arnold	Beamalloy Corp.	6360 Dublin Int'l Lane	Dublin	OH	43017-3241	(614) 766-3300
Dossick	Scott	Environmental Protection Agency, Common Sense Initiative	401 M Street, S.W.	Washington	DC	20460	(202) 260-9211
Dull	Dennis	Boeing Defense and Space Group	P.O. Box 3999, MS 82-	Seattle	WA	98124-2499	(206) 773-8855
Emurert	Patrick	U.S. Air Force, Wright Labs	WL/POOC-2	Dayton	OH	45433-7919	(513) 255-2923
Erdal	Bruce	Los Alamos National Lab	Environmental Tech Development	Los Alamos	NM	87545	(505) 667-8914
Frace	Sheila	Environmental Protection Agency, Office of Water	401 M Street, S.W.	Washington	DC	20460	(202) 260-7120
Freeman	Caroline	Occupational Safety and Health Administration	200 Constitution Ave., N.W.	Washington	DC	20210	(202) 219-7151
Gile	Steve	Environmental Protection Agency, Office of Water	401 M Street, S.W.	Washington	DC	20460	(202) 260-9817
Gillum	Danny	U.S. Marine Corps Depot		Albany	GA		(912) 439-6805
Gonzalez	Al	Corpus Christi Army Depot		Corpus Christi	TX		(512) 939-3784
Graham	Michael	BIRL, Northwestern University	1801 Maple Avenue	Evanston	IL	60201	(708) 491-5436
Gruenbaum	Peter	Boeing Defense and Space Group	P.O. Box 3999, MS 82-	Seattle	WA	98124-2499	(206) 773-8437
Haas	Karl	Cametoid Limited	1449 Hopkins St.	Whitby	Ont.	L1N 2C2	(416) 666-3400
Hirvonen	James	US Army Research Laboratory	AMSRL-MA-CC	APG	MD	21005-5069	(302) 892-6587
Horne	William G.	Empire Hard Chrome	1615 S. Kostner	Chicago	IL	60623	(312) 762-4711
Hubler	Graham	Naval Research Laboratory	Code 6671	Washington	DC	20375	(202) 767-4800
Ingle	Mark	Environmental Protection Agency, Office of Water	401 M Street, S.W.	Washington	DC	20460	(202) 260-7191
Klingenbergs	Melissa	Concurrent Technologies Corporation	1450 Scalp Ave	Johnstown	PA	15904	(814) 269-6415
Kompan	Vladimir	We Innovex, Inc.	151 S. Pfingsten Road, Unit D	Deerfield	IL	60015	(708) 291-3553
Lahe	Harvy	Husky Injection Molding	530 Queen St S.	Bolton	Ont.	L7E 5S5	(905) 951-5000
Lash	Ronald	Chrysler Corporation	800 Chrysler Drive East	Auburn Hills	MI	48326	(810) 576-7461
Legg	Keith O.	BIRL, Northwestern University	1801 Maple Avenue	Evanston	IL	60201	(708) 467-1572
Lemke	Ken	UMR Systems, Inc.	4042 Mainway	Burlington	Ont.	L7M 4B9	(905) 336-7701
Macdonald	Andrew	Torcad Limited	275 Norseman St.	Toronto	Ont.	M8Z 2A5	(905) 239-3928
Mantese	Joseph	General Motors Corporation	Bldg 1-6, 30500 Mound Road, Box 9055	Warren	MI	48090	(810) 986-2836

## Appendix C - Points of Contact

Point of Contact		Company Name	Company Address				Phone Number
Last Name	First Name		Address	City	State/Prov	Zip Code	
Manty	Brian	Concurrent Technologies Corporation	1450 Scalp Ave	Johnstown	PA	15904	(814) 269-6425
Matossian	Jesse	Hughes Research Laboratories	Loc. MA, Bldg. 250, MS RL57; 3011 Malibu Canyon Road	Malibu	CA	90265-4799	(310) 317-5121
Mattox	Donald	Management Plus, Inc.	440 Live Oak Loop	Albuquerque	NM	87122	(505) 856-6810
Melanson	Ed	Active Metal Finishing	283-285 Bering Ave	Toronto	Ont.	M8Z 3A5	(905) 233-9810
Mooney	Bill	Pure Coatings, Inc.	3301 Electronics Way	West Palm Beach	FL	33407	(407) 844-0100
Morrow	Hugh	International Cadmium Association	12110 Sunset Hills Rd, Suite 110	Reston	VA	22090	(703) 709-1400
Munson	Carter	Los Alamos National Lab	Physics Division, Mail Stop E526	Los Alamos	NM	87545	(505) 667-7509
Nastasi	Michael	Los Alamos National Lab	MS&T Division, Mail Stop K765	Los Alamos	NM	87545	(505) 667-7007
Newman	Desmond	Cametoid Limited	1449 Hopkins St.	Whitby	Ont.	L1N 2C2	(416) 666-3400
Olson	Joseph	Los Alamos National Lab	Physics Division, Mail Stop E526	Los Alamos	NM	87545	(505) 665-3193
Paeth	Richard	SK Hand Tool Corporation	3535 West 47th Street	Chicago	IL	60632	(312) 523-1300
Pearsall	Thomas	Pure Coatings, Inc.	3301 Electronics Way	West Palm Beach	FL	33407	(407) 844-0100
Phillips	Allan	Active Metal Finishing	283-285 Bering Ave	Toronto	Ont.	M8Z 3A5	(905) 233-9810
Ruffner	Heidi	Sandia National Labs	1001 University Blvd SE, Suite 100	Albuquerque	NM	87106	(505) 272-7609
Sartwell	Bruce	US Naval Research Laboratory	Code 6170	Washington	DC	20375	(202) 767-0722
Scheuer	Jay	Los Alamos National Lab	Physics Division, Mail Stop E526	Los Alamos	NM	87545	(505) 665-6525
Schmidt	Gerald	Acadian Group	6975 Davand Dr.	Mississauga	Ont.	L5T 1L5	(905) 564-1717
Schroeder	Michael	TAFA	146 Pembroke Road	Concord	NH	03301	(603) 224-9585
Shapiro	Paul	Environmental Protection Agency, Office of Research and	401 M Street, S.W.	Washington	DC	20460	(202) 260-4969
Shiwanov	Ernie	North Island Naval Depot					(619) 545-7834
Sioshansi	Piran	Spire Corporation	One Patriots Park	Bedford	MA	01730	(617) 275-6000
Sproul	William	BIRL, Northwestern University	1801 Maple Avenue	Evanston	IL	60201	(708) 491-4108
Sridharan	Kumar	University of Wisconsin	1500 Engineering Dr.	Madison	WI	53706	(608) 263-4789
Stein	Edward	Occupational Safety and Health Administration	200 Constitution Ave., N.W.	Washington	DC	20210	(202) 219-7111
Stelmack	Larry	Implant Sciences Corporation	107 Audobon Road, #5	Wakefield	MA	01880	(617) 246-0700
Stinner	Robert	ISM Technologies	9965 Carroll Canyon	San Diego	CA	92131	(619) 530-2332
Thomas	Terry	DC Chrome	348 Dewitt Road	Stoney Creek	Ont.	L8E 2T2	(905) 662-5283
Tobin	Eric	Spire Corporation	One Patriots Park	Bedford	MA	01730	(617) 275-6000
Tran	John	Pure Coatings, Inc.	3301 Electronics Way	West Palm Beach	FL	33407	(407) 844-0811
Treglio	James	ISM Technologies	9965 Carroll Canyon	San Diego	CA	92131	(619) 530-2332
Troup-Pack	Sue	Hughes Research Laboratories	Loc. MA, Bldg. 250, MS RL57; 3011 Malibu Canyon Road	Malibu	CA	90265-4799	(310) 317-5821
Troy	John	Chrysler Corporation	800 Chrysler Drive East	Auburn Hills	MI	48326	(810) 576-7376
Usherenko	Sergey		41, Platonov St	Minsk	Belarus		(0172) 328-41

**Appendix D**  
**IBP International Industry Demographics**

The following table illustrates, by country, some of the major players throughout the world who are involved in ion beam processing technologies and their particular areas of research. This list should not be considered all-inclusive, but rather demonstrates the number of international players who are pursuing advances in this technology.

Institution	Area of Study
<b>Japan</b>	
Osaka National Research Institute	Analysis of hydrogen permeation properties of TiN/TiC films deposited on martensitic steel; ion beam deposition with positive and negative ions
Kobe Steel Ltd., Material Research Laboratory	Improvement of corrosion resistance of titanium alloys by double ion implantation
Saiama Institute of Technology	Rutile and zirconia formation by oxygen direct ion implantation into sheet and thin film materials composed of Ti and Zr
Advanced Technology Ind.	Rutile and zirconia formation by oxygen direct ion implantation into sheet and thin film materials composed of Ti and Zr
Institute of Physical and Chemical Research	Rutile and zirconia formation by oxygen direct ion implantation into sheet and thin film materials composed of Ti and Zr
Kyoto University/Mitsubishi	Ion cluster beam technology
AIST(ONRI)	Ion beam deposition with positive and negative ions
Matsushita E. I. Co.	Operates a PSII system
Panasonic Matsushita	Uses IBAD to surface coat their wet dry razor blades
Kobe Steel	Major manufacturer of PVD coating systems in Japan, markets ion beam implantation technologies and sells ISM equipment in Japan
<b>China</b>	
Ion Beam Lab, Shanghai Institute of Metallurgy	Ion beam research and applications
Dalian University	Operates a PSII system; Monte Carlo simulation of energy and angle distributions of ions striking the spherical target in PSII
Textile University	Operates a PSII system
Southwest Institute of Physics	Operates a PSII system
Harbin Institute of Technology	Operates a PSII system; structure and wear behavior of nitrogen-implanted aluminum alloys
Shanghai University	Conducts IBAD research
Lanzhou University	Operates an intense beam surface treatment system
Beijing Normal	Operates several metal ion implantation systems
CCAST World Laboratory	Monte Carlo simulation of energy and angle distributions of ions striking the spherical target in PSII
<b>Korea</b>	
Korea Atomics Energy Research Institute	Triple beam implanter for industrial applications
KIST	Operates a PSII system

Institution	Area of Study
<b>India</b>	
University of Bombay, Department of Physics	Adhesion improvement of diamond and other films on various substrates by MeV ion irradiation
RSIC, Indian Institute of Technology	Adhesion improvement of diamond and other films on various substrates by MeV ion irradiation
Bhabha Atomick Res. Centre, Metallurgy Division	Adhesion improvement of diamond and other films on various substrates by MeV ion irradiation
Nuclear Science Centre	Adhesion improvement of diamond and other films on various substrates by MeV ion irradiation
University of Poona, Department of Physics	Adhesion improvement of diamond and other films on various substrates by MeV ion irradiation
IPR	Operates a PSII system
<b>Russia</b>	
Moscow State Aircraft Institute	Choice of ions and optimal modes of ion implantation of metals and alloys
State Aircraft Technical University	Modification of construction material surface by ions with low energy
State University, Omsk, and Polytechnical University, Tomsk	Influence of ion beam treatment modes on hard alloys wear resistance
Republic Engineering Technical Center	Experience of ion implantation application for hardening of details and tools in different branches of industry
Institute of Technical Chemistry, Perm, and Institute of Electrophysics, Ekaterinburg	Treatment of low density polyethylene by nitrogen ion beams
Institute of Electrophysics, Ekaterinburg, and Institute of Aircraft Materials, Moscow	Physical-chemical properties of hard alloys after ion implantation
Aircraft Technical University	Improving properties of weld joints by ion implantation
Byelorussian State University, Minsk	Modification of mechanical properties of steel as a result of double implantation
Institute of Applied Physical Problems, Minsk, and Kurchatov Institute, Moscow	Tribological properties of steel after intense pulse bombardment
Polytechnical Institute, Kharkov	Effect of nitrogen ion irradiation and following annealing on structure and physical-chemical properties
Polytechnical Institute and Steel Rolled Stock Plant, Orel	Modification of cold-upsetting tools by powerful carbon ion beam and by nitrogen ion implantation
Institute of Electrophysics and Institute of Metal Physics	Increasing stainless steel hardness by high-temperature carbon ion implantation
State University, Omsk	Surface modification of hard alloys by combined ion beams
Institute of Electrophysics and Institute of Metal Physics	Combination of ion implantation and diamond-like coating deposition for surface hardening of metals
Republic Engineering Technical Center, Tomsk	Influence of ion implantation on adhesion of metal coating deposited on polymer materials
Electrotechnical Institute of Connection, Tashkent	Modification of structure and properties of metal and insulator coatings by ion irradiation
Electrotechnical Institute of Connection, Tashkent	Ion beam modification of parameters of structures like steel-polymer coating
Tsiolkovski State Aircraft Technical University	Tribological behavior of chromium steel implanted by nitrogen
Tashkent Electrochemical Connection Institute, Institute of Electronics, Uzbek Academy of Sciences	Hardening mechanisms of surface and subsurface layers of ion implanted metals
Institute of Electronics, Uzbek Academy of	Microstructure and mechanical property modification in

Institution	Area of Study
Science	metals and alloys by ion implantation
Institute of Applied Physical Problems, Minsk	Formation of nitride phases in metals under intense ion implantation
Kurchatov Institute of Atomic Energy, Moscow and Kharkov Polytechnical Institute	Influence of ion implantation on the character of solid alloy wear
Institute of Material Resource Problem, Kiev, and Physical Institute, Moscow	Investigation of action of mean-energy nitrogen-ion beam onto the surface of composites
Physical and Technical Institute, Minsk	Ion beam implantation and friction properties of metals and alloys
Mogilev Department of Institute of Physics, Byelorussian Academy of Sciences	Transformation of structural and optical properties of polymers under ion bombardment
Aircraft Institute, Likhachev Plant, Baykov Institute of Metallurgy, Kurchatov Institute of Atomic Energy, Moscow	Study of properties of steel surfaces after ion implantation
Kurchatov Institute of Atomic Energy, Moscow	Mechanisms of alteration of deep layers of a solid under ion bombardment
Russian Scientific Center "Kurchatov Institute", Moscow and Special Design Bureau, Ekaterinburg	Wear resistance increasing of hard alloy cutting tools by ion implantation
Byelorussian State University, Minsk	High pressure regions in superhard materials implanted by high energy ions
Institute of Electronics, Uzbek Academy of Sciences, Tashkent	Nature of metals and steels surface hardening as a result of ion treatment
Institute of Organic Compositions, Moscow	Ion sputtering of copper to coat polyimide surface
Central Design Technological Bureau and Institute of Electronics, Uzbek Academy of Sciences, Tashkent	Modification of polymer surface properties by ion implantation.
Institute of Chemistry of Surface, Kiev	Optical absorption edge and a mean order in polypropylene modified by ion implantation
Institute of Chemistry of Surface, Kiev	Relationship between the structure and optical properties of polypropylene modified by implantation of fluorine ions
Institute of Chemistry of Surface, Kiev	EPA Spectra of implanted polypropylene
Ioffe Physical-Technical Institute, S. Petersburg	Inversion of conductivity type in polyimide films implanted by ions
Kuznetsov Siberian Physical Technical Institute, Tomsk	Principles of phase-structural transformations in metallic alloys under high-dose ion implantation
Institute of Nuclear Physics, Tomsk	Non-traditional methods of pulse-periodic ion-beam and plasma-ion treatment of materials
Institute of Chemistry of Surface, Kiev	Increasing of polymer electroconductivity caused by molecular ion implantation
Byelorussian State University, Minsk	Ion implantation of polymer films
Institute of Strength Physics and Materials Science of RAS	Mechanisms of long range effect in metals and alloys by ion implantation
Tomsk State Academy of Architecture and Building	Mechanisms of long range effect in metals and alloys by ion implantation
Russian Academy of Sciences	Mechanisms of long range effect in metals and alloys by ion implantation
MAI	High power ion beam treatment application for properties modification of refractory alloys
VIAM	High power ion beam treatment application for properties modification of refractory alloys

Institution	Area of Study
Nuclear Physics Institute	High power ion beam treatment application for properties modification of refractory alloys
Moscow Aviation Institute	Surface modification of superalloys and heat resistant steels by irradiation of low and high energy ion beams
High Current Electronics Institute	Vacuum arc sources
<b>Belarus</b>	
Byelorussian State University	Industrial applications of ion implantation
BSPA Minsk	Operates a PSII system
<b>Poland</b>	
Soltan Institute for Nuclear Studies	Use of metallic plasma pulses in formation of thin coatings on melted surfaces of substrates
<b>UK</b>	
AEA Technology	Evaluation of mechanical test methods for coatings, thin films and ion implanted surfaces; mechanical properties of steel using low energy, high temperature nitrogen ion implantation
RCSE, University of Hull	Evaluation of mechanical test methods for coatings, thin films and ion implanted surfaces
School of Materials, University Newcastle-upon-Tyne	Evaluation of mechanical test methods for coatings, thin films and ion implanted surfaces
School of Industrial and Manufacturing Science, Cranfield University	Evaluation of mechanical test methods for coatings, thin films and ion implanted surfaces
Imperial College	Industrial awareness and applications of ion implantation as an effective surface treatment
University of Surrey	Operates a PSII system
University of Birmingham	Significance of nitrogen mass transfer mechanism on the nitriding behavior of austenitic stainless steel
Culham Laboratory	
Tech-ni-plant	Involved in nitrogen implantation into chrome plated plastic molds using systems made by TecVac
TecVac	Manufactures direct nitrogen ion implantation systems. Offer two systems for sale: the Tecvac 221, with an output of three milliamperes (mA) and one with an output of 45 mA, based on a magnetic "bucket" design.
Whickham Ion Beam Systems Ltd.	Produce beamline systems that can generate up to 10 milliamperes of nitrogen, 6 milliamperes of chromium and lesser amounts of other metals
<b>France</b>	
Lab de Metallurgie Physique, Univ Poitiers	Texture of IBAD thin TiN films in dependence on the ion beam intensity and angle of incidence
Institute de Physique Nucleaire de Lyon, University	Study of BN formation by dual implantation of boron and nitrogen in bearing steel
Institute de Recherche sur la Catlysa CNRS	Study of BN formation by dual implantation of boron and nitrogen in bearing steel
TURBOMECA	High power ion beam treatment application for properties modification of refractory alloys
SEP	Surface modification of superalloys and heat resistant steels by irradiation of low and high energy ion beams
Lab de Metalurgie Physique URA 131 CNRS, Univ Poitiers	Characterization and wear behaviour of SiC coatings prepared by ion beam assisted deposition
<b>Spain</b>	

Institution	Area of Study
INASMET Organization, in San Sebastian	Changes in tribological properties of stainless steel after ion implantation of carbon at very high doses
Department de Fisica de Materiales, University Pais Vasco	Electronic stopping of slow ion in solids
ICM, Dpto, Fisica Aplicada C-XII, Univ. Autonoma de Madrid	Zr-BN multilayers obtained by ion assisted sputtering; depth profile characterization
UTRC-MSTE	Changes in tribological properties of stainless steel after ion implantation of carbon at very high doses
AIN	Industrial awareness and applications of ion implantation as an effective surface treatment
CNPlasma	
<b>Portugal</b>	
ITN Dept. Fisica	Formation of Al <sub>3</sub> Cr <sub>2</sub> intermetallic phase by Cr ion implantation
FCUL Department	Formation of Al <sub>3</sub> Cr <sub>2</sub> intermetallic phase by Cr ion implantation
DFNUL	Formation of Al <sub>3</sub> Cr <sub>2</sub> intermetallic phase by Cr ion implantation
National Institute for Industrial Technology and Engineering	Ion beam mixing of chromium or zirconium films with sapphire
University of Lisbon	Ion beam mixing of chromium or zirconium films with sapphire
<b>Italy</b>	
Dipt. Ingegneria Nucleare, Politecnico di Milano	Phase formation and amorphization processes
Dipt. di Fisica, Univ. Trento and INFM	Metal-ceramic ion-beam mixing; analysis of hydrogen permeation properties of TiN/TiC films deposited on martensitic steel
CMBM Ins. Trentino di Cultural	Analysis of hydrogen permeation properties of TiN/TiC films deposited on martensitic steel
ENEA, Fusion Sector CRE Brasimone	Analysis of hydrogen permeation properties of TiN/TiC films deposited on martensitic steel
Institute for Advanced Materials, Ispra , Joint Research Centre	Influence of Yttrium ion implantation on the oxidation behaviour of PM chromium
<b>Denmark</b>	
Institute of Physics and Astronomy, Aarhus University	Ion bombardment of nanoparticle coatings
DANFYSIK A/S	Produce beamline systems that can generate up to 10 milliamperes of nitrogen, 6 milliamperes of chromium and lesser amounts of other metals
Danish Technological Institute	Ion implanters for surface modification of metals
Tribology Centre, DTI	Ion implantation implementation
<b>Netherlands</b>	
Dept. of Atomic and Interface Physics, Utrecht University	Nitrogen diffusion during implantation in nickel/iron bilayers
<b>Finland</b>	
VTT Manufacturing Technology	Barometer of plasma and ion assisted surface modification methods
VTT Electronics	Barometer of plasma and ion assisted surface modification methods
<b>Sweden</b>	

Institution	Area of Study
Ins. of Technology, Uppsala Univ.	Re-sputtering effects during ion beam assisted deposition
<b>Belgium</b>	
Department of Metallurgy and Materials Engineering (MTM)	Carbonaceous surface layers deposited on TiN coatings by ion implantation
Institute for Nuclear and Radiation Physics (IKS)	Carbonaceous surface layers deposited on TiN coatings by ion implantation
<b>Germany</b>	
University of Heidelberg	Ion bombardment research for corrosion studies; texture of IBAD thin TiN films in dependence on the ion beam intensity and angle of incidence
Ins. for Physikalische Chemie and Elektrochemie, University Heinrich, Heine	Electrochemical and surface analytical characterization of radiation effect after N2 implantation into Al and Al2O2
Forschungszentrum Julich	Texture of IBAD thin TiN films in dependence on the ion beam intensity and angle of incidence; electrochemical and surface analytical characterization of radiation effect after N2 implantation into Al and Al2O2
Fraunhofer Ins. fur Festkorperchnologie	Texture of IBAD thin TiN films in dependence on the ion beam intensity and angle of incidence
Physikalisch-Chemisches Ins., University of Heidelberg	Texture of IBAD thin TiN films in dependence on the ion beam intensity and angle of incidence
University Augsburg, Ins. for Physik	Ion beam assisted deposition of superhard materials
Technical University, Dresden, Institute of Analytical Chemistry	Post-treatment of amorphous carbon films with high energy ions
RCR	Operates a PSII system
I A Physics	Operates a PSII system
Institute Nuclear and Solid State Physics	
Research Center Rossendorf Inc.	50 kV pulse generator for plasma source ion implantation; PSII of oxygen and nitrogen in aluminum
Puls-Plasmatechnik GmbH	50 kV pulse generator for plasma source ion implantation
<b>South Africa</b>	
Physic Department, University of Pretoria	Damage ranges in metals after ion implantation
AEC South Africa	Operates a PSII system
University of Natal	Operates a PSII system; calculated the ion-matrix sheath around a square bar; modeling of a plasma consisting of two species of cold collisionless ion fluids for PSII
Material Technology, Atomic Energy Corporation of South Africa	Nitrogen profiles of high dose, high temperature PSII treated austenitic stainless steel
<b>Brazil</b>	
Institute de Fisca, UFRGS	Low temperature nitride phase transformation induced by ion beams
<b>USA</b>	
University of Tennessee	Operates a PSII system; ion beam mixing of chromium or zirconium films with sapphire; enhanced pitting corrosion resistance of 304L stainless steel by PII
Institute for Materials Science, George Washington University	Interface mixing of energetic metals deposited on metals
Colorado State University, Department of Mechanical Engineering	High-current density, broad -beam, metal-ion implantation for tribological applications
Colorado School of Mines, Physics Department	High-current density, broad -beam, metal-ion implantation for tribological applications
Northeastern University	Operates a PSII system; plasma immersion ion implantation

Institution	Area of Study
Highlands University	doping experiments for microelectronics
Plasma Assisted Materials Processing Laboratory, Department of Electrical Engineering and Computer Sciences, University of California	Operates a PSII system
Applied Physics Department, Cornell University	Analytical modeling of plasma immersion ion implantation target current
Department of Physics, West Virginia University	Magnetic insulation of secondary electrons in plasma source ion implantation; ion-beam-induced densification of sol-gel ceramic thin films
Arizona State University	Ion-beam-induced densification of sol-gel ceramic thin films
<b>Canada</b>	
Physics Department, Queens University	Calculated the ion-matrix sheath around a square bar; modeling of a plasma consisting of two species of cold collisionless ion fluids for PSII
<b>Australia</b>	
Department of Electronic Materials Engineering, Australian National University	Ion-beam-induced densification of sol-gel ceramic thin films
Australian Nuclear Science and Technology Organization	Mixing and corrosion in Ni implanted with Pt through a sacrificial layer of alumina
Department of Materials Engineering, University of Wollongong	Operates a PSII system; surface mechanical properties of PI3 treated samples by instrumented indentation; measurements of potentials and sheath formation in plasma immersion ion implantation; significance of nitrogen mass transfer mechanism on the nitriding behavior of austenitic stainless steel
	Titanium aluminide formation in Ti implanted aluminum alloy; significance of nitrogen mass transfer mechanism on the nitriding behavior of austenitic stainless steel

**Appendix E**  
**Successful IBP Technology Demonstrations**

**E.1 Nitrogen Ion Implantation Successful Demonstrations**

Application Area	Tool Material	Application	Lifetime Increase	Additional Benefits
Cutting Tools	WC/Co	Rubber Slitting Knives	12x	Friction Reduced 30%
	WC/Co	Sheet Steel Chopper Blades	3x	Reduced Chipping
	4% Ni, 1% Cr Steel	Tool Inserts	2x	Reduced Tool Corrosion
	M2	Tobacco Knives	4x	Improvement Remains After Sharpening
	H13 Steel	Guillotine Blades For Ti Rod	2x	Reduced Build-Up at Edge
	M2	9mm Reamer For Steel	6x	High Tolerance Maintained
	M2	Pilot Pins; .002 in. 302 Stainless Steel	5x	
	440C Stainless Steel	Retainers; Hydraulic Pump Parts For Light Aircraft		Abrasive Wear Greatly Reduced
	Chrome Plate (M2)	Taps; Tapping Cold-Rolled Steel (Garden Hose Couplings)	8x	
	Chrome Plate (S7)	Unscrewing Cores; Injection Molding Bottle Caps	> 3x	Wear From Rubber Water Seals Reduced
	Tool Steel	Steel Slitter Blades	4x	
	Alumina	Aluminum Cutter Inserts	2x	
	M1	Steel Drills	2x	
	M2	Steel Cut-Off Tools	3x	
	M2	Steel Thread Dies	5x	
	WC	Graphite Drills	6x	
	D2	Paper Slitter Blades	2x	
	WC	Fiberboard Cutter Inserts	2x	

Application Area	Tool Material	Application	Lifetime Increase	Additional Benefits
Forming Tools	D3 Steel	Forming Tools	3x	Greatly Reduced Adhesive Wear
	D2 Steel	Forming Die For Aluminum Can Bottoms	3x	Markedly Reduced Pick-Up
	WC/Co	Wire Dies	5x	Improved Surface Finish
	WC/Co	Punch and Die Sets For Sheet Steel	4-6x	Improvement Remains After Resharpening
	S7	Compacting Punches; Bronze Powder	6x	
	D2 (Nitrided)	Compacting Punches and Die; Compounding Mineral-Filled Epoxy	2.5x	
	D2	Draw Die; Drawing .034 in. 305 Stainless Steel (Electronic Can)	> 15x Before Polishing	Galling Reduced
	Chrome Plate (D2)	Draw Punches; Ironing .125 in. 4140 Hot-Rolled Steel	5x	
	Carbide	High-Speed Stamping Dies; .016 in. Phosphor Bronze (Electronic Connectors)	3x	
	Chrome Plate (P20)	Mold Cavities; Injection Molding 20% Glass Fiber-Reinforced Polyester (Auto Parts)	> 10x	
	Chrome Plate (A2)	Mold Cavities; Injection Molding Phenolic (50% Glass + Mineral Filled)	10x	
	M2	Pierce Punches; 1/2 in. Hot-Rolled Steel	12x	
	M2	Pierce Punches and Dies; .1 in. CA110 Copper (Starting Motor Contacts)	4x	
	D2, M2	Slide-Forming Dies; .012 in. 1074 Spring Steel (Electrical Clips)	10x	
	S5	Tablet Compacting Punches; Compacting Pharmaceutical Powder (Ibuprofen)		Sticking Reduced
	WC	Steel Wire Dies	4x	
	Chrome Plate, 01	Steel Wire Guides	4x	
	H13	Copper Mill Rolls	2-5x	Improved Finish
	ASP-23, A2, D2	Aluminum Scoring Dies	3-6x	
	WC	Steel Swaging Dies	2x	
	Carburized Steel	Steel Forming Tools	3x	

Application Area	Tool Material	Application	Lifetime Increase	Additional Benefits
Forming Tools (continued)	WC	Steel Deep Draw Dies	2x	
	D2	Powdered Metal Compacting Punches	2x	
	D2	Aluminum Forming Punches	Reduced Pick-Up	
	M2	Spring Steel Punches	2x	
	M2, D2, WC	Titanium Punches and Dies	2-5x	
	WC	Silicon Steel Punch and Die Sets	5x	
	Chrome Plate	Copper Flaring Tools	4x	

Application Area	Tool Material	Application	Lifetime Increase	Additional Benefits
Non-Metallic Applications	WC	Enamel Dental Burrs	3-5x	
	WC	Tin Plate Sleeves	5x	Easier Stripping
	P20 Steel	Profile Die For Plastic Extrusion	4x	Improved Surface Finish
	Diamond Tools	Plastic Cutting	4x	Quality Maintained
	Tool Steel	Nitrided Steel Molds	2x	Combination Better Than Either Process Alone
	Nitrided Tool Steel H13	Calibrator Die	3x	Accuracy Maintained
	420 Stainless Steel	Plastic Calibrator Dies; Shaping Extruded Vinyl Siding	2x	
	D2, S7	Plastic Injection Molding Nozzles	2x	
	D2, S7	Plastic Injection Molding Gates	2x	
	Tool Steels	Plastic Injection Mold Feed Screws	2-10x	
	Tool Steel	Plastic Molds; Nylon	3x	Improved Corrosion Resistance
	S7	Plastic Molds		Better Release
	D2	Acetate Punches	2x	
	WC	Rubber Slitter Blades	10x	
	M2	Phenolic Resin Thread Taps	10x	
	WC	P.C. Epoxy Board Drills	2-3x	
	Diamond	Plastic Cutting Tools	2x	

## E.2 Metal Ion Implantation Successful Demonstrations

Application Area	Tool Material	Application	Lifetime Increase	Additional Benefits
Aerospace		Jet Engine Bearings	2.5x	
Cutting Tools	WC/Co	Drilling Tool Inserts	2.2x	
	WC/Co End Mill	Milling Tool Inserts	3.75x	1.5x Cutting Rate
	WC/Co	Threading Tool Inserts	2.85x	
	Ti/N Coated WC/Co	Turning Tool Inserts	2.5x	1.58x Cutting Rate
	Ti/N Coated WC/Co	Turning Tool Inserts	1.67x	1.5x Cutting Rate
	Ti/N Coated WC/Co	Grooving Tool Inserts	2x	1.43x Cutting Rate and 2x Depth of Cut
	WC/Co	Turning Tool Inserts	3x	Improved Surface Finish

## Appendix F

### Environmental Costs Not Incurred In The Use of Ion Beam Processing Technologies

#### F.1 Introduction

The cadmium and chromium electroplating industry is subject to worker health and safety regulations as well as media-specific environmental regulations for air, water, and solid waste, and multimedia regulations being developed under EPA's Common Sense Initiative. The industry incurs a number of costs in order to comply with these stringent regulations which are outlined below. Much of these costs result from the treatment and disposal of wastewater and sludge generated during the plating process and from the disposal of spent plating baths. Some costs are incurred to comply with worker safety and health regulations which pertain to the control of ambient concentrations of contaminants at the work place. None of these costs are incurred by the ion beam surface finishing industry because this industry does not use cadmium and chromium compounds in ways that result in contamination. This appendix provides an overview of the regulations affecting the cadmium and chromium electroplating industry and presents several independent estimates of the costs which are incurred by this industry to comply with these regulations.

#### F.2 Regulations

##### F.2.1 Worker Health and Safety Regulations

Many of the people contacted in the site visits indicated that worker health and safety regulations promulgated by the Occupational Health and Safety Administration (OSHA) were the most important driver for emissions controls. OSHA has promulgated standards for worker exposure called permissible exposure limits (PELs). PELs regulate the concentration of a given substance that may be present in the air inhaled by workers.

OSHA completed a major revision of PELs in 1989 (54 FR 2332; January 19, 1989), but the revision was overturned by the U.S. Court of Appeals for the Eleventh Circuit in 1992 [*AFL-CIO v. OSHA*, 965 F.2d 962 (11th Cir., 1992)]. OSHA revoked the 1989 PELs on June 30, 1993, and reinstated the previous limits (58 FR 35338; June 30, 1993). OSHA is considering reinstating the 1989 PELs for a subset of the original 1989 list of substances. Chromium compounds are not included in this effort (Conversation with Edward Stein, February 1, 1996). The Oil, Chemical, and Atomic Workers International Union and Public Citizens' Health Research Group petitioned OSHA on July 19, 1993, for an emergency temporary standard of 0.5 ug/l as an eight hour time weighted average for hexavalent chromium. OSHA denied the request due to lack of sufficient data, but is working on a rulemaking regarding the regulation of hexavalent chromium. A proposed rule is expected by the end of 1996, but the effort might be delayed due to budget considerations (Conversation with Edward Stein, February 1, 1996).

Table 1 lists the current and vacated 1989 PELs as well as the limits recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). OSHA frequently models PELs on recommendations of the ACGIH. All standards are based on an eight hour time weighted average (TWA).

**Table 1. Hazardous Material PELs (Airborne)**

Air Contaminant	Current PEL	Vacated 1989 PEL	ACGIH TLV
Chromic acid and chromates	0.1 mg/m <sup>3</sup>	0.1 mg/m <sup>3</sup>	0.05 mg/m <sup>3</sup>
Chromium (II) compounds	0.5 mg/m <sup>3</sup>	n/a	0.5 mg/m <sup>3</sup>
Chromium (III) Compounds	0.5 mg/m <sup>3</sup>	n/a	0.5 mg/m <sup>3</sup>
Chromium (VI) compounds, sol.	n/a	n/a	0.05 mg/m <sup>3</sup>
Chromium (VI) compounds, certain insol.	n/a	n/a	0.05 mg/m <sup>3</sup>
Chromium (VI) compounds, certain insol.	n/a	n/a	0.01 mg/m <sup>3</sup> Proposed
Chromium (VI) compounds			0.0005 mg/m <sup>3</sup> proposed by Petitioners
Chromium, sol. chromic, chromous salts	n/a	0.5 mg/m <sup>3</sup>	0.5 mg/m <sup>3</sup>
Chromium metal and insol. salts	1 mg/m <sup>3</sup>	1 mg/m <sup>3</sup>	no change
Cadmium compounds (including dust and fume) (29 CFR 1910.1027)	0.005 mg/m <sup>3</sup>	n/a	n/a

PEL = permissible exposure limit for 8-hr TWA

TLV = threshold limit value

ACGIH = American Conference of Government Industrial Hygienists

#### **F.2.2 Water Regulations**

The Clean Water Act regulates direct discharges to Waters of the United States and indirect discharges to sewage treatment plants or publicly owned treatment works (POTW). Direct dischargers are subject to the National Pollutant Discharge Elimination System (NPDES). Indirect dischargers are subject to federal pretreatment standards and other pre-treatment standards imposed by state or local governments. Facilities that existed prior to July 1, 1977, are considered existing, those built after that date are considered new. Electropolaters may be subject to the effluent limitations listed under the Electroplating Point Source Category at 40 CFR §413 or the Metal Finishing Point Source Category at 40 CFR §433. The effluent limitations that apply depend on three factors:

- Whether the facility is a direct or an indirect discharger;
- Whether the facility is new or existing; and
- Whether the facility is a captive shop which owns more than 50% (annual area basis) of the materials undergoing metal finishing or a job shop.

Table 2 lists the pretreatment standards for the Electroplating Point Source Category and Table 3 lists the pretreatment standards for the Metal Finishing Point Source Category.

**Table 2. Pretreatment Standards for the Electroplating Point Source Category**

Pollutant	Facilities Discharging <10,000 gpd		Facilities Discharging >10,000 gpd	
	Daily Maximum (mg/l)	Max. 4 Day Average (mg/l)	Daily Maximum (mg/l)	Max. 4 Day Average (mg/l)
Cadmium	1.2	0.7	1.2	0.7
Chromium	N/A	N/A	7.0	4.0
Cyanide	5.0	2.7	1.9	1.0
Total Metals	N/A	N/A	10.5	6.8

**Table 3. Pretreatment Standards for the Metal Finishing Point Source Category**

Pollutant	Existing Sources		New Sources	
	Daily Maximum (mg/l)	Monthly Average (mg/l)	Daily Maximum (mg/l)	Monthly Average (mg/l)
Cadmium	0.69	0.26	0.11	0.07
Chromium	2.77	1.71	2.77	1.71
Cyanide	1.20	0.65	1.20	0.65

The Pretreatment standards for large electroplating facilities and new metal finishing facilities include limits for cyanide that are either at or below the detection limit for some EPA-approved test methods based on titration (*Environmental Testing and Analysis*. Volume 5, No.2. February 1996). Colorimetric methods must be used to test for cyanide at these facilities at potentially greater expense.

States, local governments, and Indian Tribes may impose water quality based standards on direct dischargers to protect designated uses, such as fishing or swimming, for a body of water. These water quality based standards are added to the NPDES or pretreatment requirements and may be more stringent than those requirements. States and local governments are not prohibited from imposing more stringent effluent limitations than those specified by EPA on both direct and indirect discharges.

#### **F.2.2.1 New Requirements**

EPA Administrator Carol Browner introduced the Common Sense Initiative (CSI) in 1994. The goal of CSI is to incorporate flexibility and innovation into environmental regulation in order to achieve better environmental results for a given investment by industry. EPA has convened representatives from federal, state, and local governments, community and national environmental groups, environmental justice groups, labor, and industry to examine the regulatory requirements impacting six pilot industries. The Metal Finishing industry is one of the pilot industries and EPA is developing regulations for the Metal Products and Machinery (MP&M) category under the CWA in the context of CSI.

The MP&M category covers facilities that “manufacture, rebuild, and maintain finished metal parts, products, or machines.” Electroplating is one of 47 unit operations covered by the rule which may overlap with and eventually replace the Metal Finishing Point Source Category. EPA published the proposed Phase I Metal Products and Machinery rule on May 30, 1995 (60 FR 28209). Phase I covers sources in the aerospace, aircraft, hardware, electronic equipment, ordnance, mobile industrial equipment, and stationary industrial equipment industries. EPA estimates that more than 10,000 sources could be affected by Phase I, with about 85% indirect dischargers and 15% direct dischargers. Phase II will cover sources in the motor vehicle, office equipment, railroad, precious metals, household appliances, bus and truck, instruments, and shipbuilding industries. New sources and existing sources with a combined process wastewater discharge of one million gallons per year or more will be subject to the concentration limits for cadmium, chromium, and cyanide listed in Table 2 (from proposed MP&M rule). These new concentration limits are shown in Table 4 below.

**Table 4. New Concentration Limits Per Proposed MP&M Rule**

Pollutant	Daily Maximum - mg/l	Monthly average - mg/l (may not exceed this value)
Cadmium	0.7	0.3
Chromium	0.3 (currently 2.77)	0.2 (currently 1.71)
Cyanide	0.03	0.02

#### **F.2.2.2 Centralized Waste Treatment**

EPA proposed regulations for centralized waste treatment (CWT) facilities on January 27, 1995 (60 FR 5464). CWT facilities are facilities that receive waste from off-site for treatment. According to Bill Sonntag, director of government affairs for the American Electroplaters and Surface Finishers Society, many companies in the metal finishing industry rely on CWT facilities to treat certain wastes. These wastes include treatment residues, tank bottoms, and peak flows exceeding on-site capacity. EPA estimates that the cost of compliance with the proposed rule would be about \$2 million per facility. Annual operating and maintenance costs would increase by about \$800,000 per facility. EPA also estimates that about 15% of CWTs would go out of business and up to 35% would be at risk of going out of business as a result of the regulations. Increased costs for waste treatment and fewer CWT facilities available for treatment of electroplating wastes would increase the costs of cadmium and chromium electroplating. (Plating and Surface Finishing, July 1995, pp.30-31)

#### **F.2.3 Air Regulations**

Title III of the Clean Air Act Amendments of 1990 addresses the emissions of hazardous air pollutants (HAP). The list of 189 HAPs established by EPA includes cadmium and chromium compounds. Affected sources have been assigned source categories by EPA and a timetable for the promulgation of national emission standards for hazardous air pollutants (NESHAP) was published on December 3, 1993. EPA promulgated National Emission Standards for Chromium Emissions From Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks on January 25, 1995 (60 FR 4947). The deadline for promulgation of the NESHAP for the Miscellaneous Metal Parts and Products subcategory of the Surface Coating Processes category is November 15, 2000.

The Chromium Electroplating NESHAP regulates both small and large, major and minor sources. Major source emit 10 tons per year (tpy) of a single HAP or 25 tpy of a combination of HAPs. For the purposes of the Chromium Electroplating NESHAP, small sources must have a maximum cumulative potential rectifier capacity below 60 million ampere-hours per year. Existing hard chromium plating tanks at small, hard chromium electroplating facilities must meet an emissions limit of 0.03 mg/l, based on the performance of a packed-bed scrubber. All new hard chromium tanks and existing hard chromium tanks located at large, hard chromium electroplating facilities must meet an emissions limit of 0.015 mg/l, based on the performance of a composite mesh-pad system. All decorative chromium tanks and chromium anodizing tanks at new and existing facilities must meet an emissions limit of 0.01 mg/l or must have a surface tension that does not exceed 45 dynes per cubic centimeter, based on the use of fume suppressants. There is no emissions limit for decorative chromium tanks using trivalent chromium, but the operators of these tanks must follow certain work practice requirements.

#### **F.2.4 Solid Waste Regulations**

Several wastes associated with the electroplating industry are listed hazardous wastes in 40 CFR §261.31 of the regulations implementing the Resource Conservation and Recovery Act (RCRA). The following are examples of such wastes:

- F006 - Wastewater treatment sludges from electroplating operations, except for certain sludges associated with aluminum, tin, and zinc plating operations;
- F007 - Spent cyanide plating bath solutions from electroplating operations;
- F008 - Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process;
- F009 - Spent stripping and leaning bath solutions from electroplating operations where cyanides are used in the process.

In addition to listed wastes, chromium and cadmium plating operations may generate characteristic hazardous wastes that exhibit the characteristics of ignitability, reactivity, corrosivity, or toxicity according to 40 CFR §261.20 *et. seq.*

RCRA imposes stringent requirements on generators of hazardous wastes. Generators are responsible for the proper storage, transportation, treatment, and disposal of the wastes they generate.

#### **F.2.5 Foreign Regulations**

Foreign regulations governing cadmium and chromium may also be a consideration in certain markets. In some cases, foreign regulations are more stringent than those in the U.S. In Germany, the limit for cadmium in ambient air is 0.04  $\mu\text{g}/\text{m}^3$ , more than two orders of magnitude less than the OSHA standard. The limit for cadmium in wastewater for coating operations is 0.1 mg/l, three times more stringent than the monthly average proposed in EPA's MP&M rulemaking (Risk Reduction Monograph No. 5: Cadmium; Organization for Economic Co-operation and Development; 1994).

#### **F.3 Cost**

This section presents several independent estimates of the costs which are incurred by the cadmium and chromium electroplating industry resulting from the regulations outlined above, which are not incurred by the ion beam surface finishing industry.

##### **F.3.1 Industry Cost Estimate**

Bill Sonntag, Director of Government Relations for NAMF and AESF, estimated that the metal finishing industry has spent \$42 million, or 27% of capital expenditures on pollution prevention. He estimates that the industry has spent \$218 million, or about 5.7% of sales, on pollution control (minutes of the January 19, 1995 Metal Finishing Subcommittee of EPA's Common Sense Initiative)

###### **F.3.1.1 Worker Safety and Health**

OSHA prepared a cost estimate for compliance with its proposed PEL of 5 :g/m<sup>3</sup> on February 6, 1990 (55 FR 4052). OSHA estimated that the cost of compliance with the proposed PEL would be \$194,700 for the industry and \$470,700 for all of the electroplaters working in the industry, for a total of \$665,400 in 1987 dollars. OSHA determined that there are approximately 1,166 shops electroplating predominantly with cadmium. OSHA estimated that the costs would be \$200 per plant and \$78 per employee representing about 7.59% of the profit of the average electroplating shop. A price increase of 0.33% on shop products would be necessary to recover the costs of compliance. OSHA indicated that exposures were already low in most plating shops and that resulted in very low cost estimates for compliance with the proposed (now final) PEL of 5 :g/m<sup>3</sup>.

###### **F.3.1.2 Environmental**

EPA estimated the cost of compliance for MP&M Phase I sites in 1989 dollars using the MP&M Design and Cost Model. EPA chose 396 model sites for development of the cost model based on whether the sites generated revenue from an MP&M Phase I sector, discharged wastewater, and supplied sufficient economic

and technical data required to estimate compliance costs and assess cost effectiveness of the technology options. Wastewaters that were contract hauled off site, deep-well injected, or discharged to septic systems were not included in the model. The model uses survey weights to project estimates from the model sites to the 10,601 identified MP&M Phase I sites. Separate cost estimates were made using each of five sets of treatment technology options.

Option 1 is end-of-pipe treatment and includes the following technologies:

- Chemical precipitation and sedimentation (including sludge dewatering using gravity thickening, and pressure filtration);
- Oil/water separation through chemical emulsion breaking and either skimming or coalescing;
- Cyanide destruction through alkaline chlorination;
- Chemical reduction of hexavalent chromium;
- Chemical reduction of chelated metals; and
- Contract hauling of solvent degreasing wastewaters.

Option 2 is end-of-pipe treatment and in-process source reduction and recycling. Option 2 is EPA's preferred option for direct dischargers and includes the following technologies:

- The technologies included for Option 1;
- Flow reduction with flow restrictors, conductivity controllers or timed rinses, and countercurrent cascade rinsing for all flowing rinses;
- Flow reduction through manual control of the wastewater discharge rate or through analytical testing and maintenance of bath chemistry for all other process water-discharging operations;
- Centrifugation and 100 percent recycling of painting water curtains;
- Centrifugation and pasteurization to extend the life of water-soluble machining coolants, reducing discharge volume by 80 percent; and
- In-process metals separation and revere with ion exchange followed by electrolytic recovery of the cation regenerants for selected electroplating rinses. This includes first-stage drag-out rinsing (when necessary) with electrolytic metal recovery. These technologies were not applied to chromium electroplating rinses because chromium is not amenable to electrolytic recovery.

Option 1A is a tiered option for "low" flow and "high" flow sites which was established only for indirect dischargers. "Low" flow sites are defined as sites with a discharge volume of less than 1,000,000 gallons per year. "Low" flow sites would be required to comply with the concentration-based standards of Option 1. "High" flow sites have a discharge volume of greater than 1,000,000 gallons per year and would be required to comply with the mass-based standards of Option 2.

Option 2A is end-of-pipe treatment and in-process source reduction and recycling for "high" flow sites. This option was established for indirect dischargers and is EPA's preferred option for indirect dischargers. Option 2A requires "high" flow indirect sites to comply with the mass-based standards of Option 2. Existing "low" flow indirect sites would be exempt from the standards and new indirect sites would be required to comply with the mass-based standards of Option 2.

Option 3 is advanced end-of-pipe treatment and recycling. Option 3 includes the technologies of Option 2 plus end-of-pipe ion exchange with 90% reuse of treated wastewater.

The cost estimates developed by EPA as part of the MP&M Phase I rulemaking apply to all sources in Phase I, not just electroplaters. Because the cost estimates are based on technology options that could be appropriate for electroplating, they are a useful source of compliance cost data for Cd and Cr electroplating. In the CAI Engineering study discussed below, 58% of the zero discharge shops were small hard chrome plating shops. The study states that "the hard chrome process is one of the easiest to operate as a close-loop." (CAI Engineering study, p.20) Only 8% of all shops in the study achieved zero discharge, but it is

important to note that zero discharge facilities did not meet the criteria to be included in the development of the MP&M Design and Cost Model.

Table 5a contains the cost estimates developed by EPA using the MP&M Design and Cost Model. Table 5b contains the same cost estimates divided by the 10,601 sites. Option 2 is EPA's preferred option for direct dischargers and Option 2A is the preferred option for indirect dischargers.

**Table 5a Results of EPA's MP&M Design and Cost Model  
(adapted from Table 12-1 in the development document)**

Option Number	Indirect Dischargers		Direct Dischargers	
	Total Capital Investment (millions of 1989 dollars)	Operating, Maintenance, and Monitoring (millions of 1989 dollars)	Total Capital Investment (millions of 1989 dollars)	Operating, Maintenance, and Monitoring (millions of 1989 dollars)
1	277	267	45.9	14.8
2	433	241	59.0	13.1
3	1,160	677	148	88.4
1A	434	236	N/A	N/A
2A	337	145	N/A	N/A

**Table 5b Results of EPA's MP&M Design and Cost Model Per Facility  
(adapted from Table 12-1 in the development document)**

Option Number	Indirect Dischargers		Direct Dischargers	
	Total Capital Investment (thousand 1989 dollars)	Operating, Maintenance, and Monitoring (thousand 1989 dollars)	Total Capital Investment (thousand 1989 dollars)	Operating, Maintenance, and Monitoring (thousand 1989 dollars)
1	26.1	25.2	4.3	1.4
2	40.8	22.7	5.6	1.2
3	109.4	63.9	14.0	8.3
1A	40.9	22.3	N/A	N/A
2A	31.8	13.7	N/A	N/A

### F.3.1.3 CAI Engineering Study

The National Center for Manufacturing Sciences published *Pollution Prevention and Control Technology for Plating Operations*, a study which evaluates pollution prevention and pollution control technologies used in electroplating operations in 1994. A survey of active electroplating shops was made to support the study, which was conducted by George Cushnie of CAI Engineering. The study includes cost information for end-of-pipe pollution control equipment, among other things. Table 6 shows the median and mean capital and annual operating costs for the end-of-pipe pollution control equipment at 184 electroplating shops which have chromium and cadmium electroplating facilities and which responded to the survey. These data represent the cost of wastewater and sludge treatment resulting from all operations at each of the 184 electroplating shops.

**Table 6. Cost Data for End-of-Pipe Treatment Equipment at Cd and Cr Electroplating Shops From CAI Engineering Study of Electroplating Industry**

Statistical Parameter	Initial Capital Cost (1993 dollars)	Annual Operating Cost (1993 dollars)
Median	\$164,596	\$47,370
Mean	\$295,025	\$86,988
Sample Size	130	155

The data for initial capital cost represent only the initial capital purchase and do not include the cost of additional control equipment purchased subsequently. In order to facilitate comparison, all costs were converted to 1993 dollars using the Chemical Engineering Plant Cost Index published monthly in *Chemical Engineering* magazine.

The costs for end-of-pipe treatment were included in this study because they are not recoverable by the electroplating shop and they are costs which are not incurred by facilities using ion beam surface finishing technologies. The costs associated with pollution prevention and recycling for the electroplating shops were not included because these costs are at least partially offset by savings from reduced usage of process chemicals and reduced waste treatment and disposal costs.

#### F.3.1.4 Other Costs

Waste treatment and disposal costs are commonly considered the highest added costs for using electroplating for metal finishing applications. There are, however, unique factors associated with electroplating that can be more costly than waste treatment and disposal. Dr. Peter Gruenbaum, with the Comprehensive Chemical Reduction Program at Boeing's defense group, has prepared a cost-benefit analysis for chromium electroplating and its alternatives. Dr. Gruenbaum has determined that post-plate grinding and masking represent a significant portion of the cost of chromium electroplating, exceeding the cost of waste treatment and disposal. His estimates were made in Boeing's newest plating facility which utilizes state-of-the-art waste reduction equipment and techniques. Keith Lash at Northwestern University has independently reported similar cost information for chromium electroplating, according to Dr. Gruenbaum. Table 7 shows the results of Dr. Gruenbaum's cost-benefit study.

**Table 6. Results of Boeing Cost-Benefit Study of Chromium Electroplating**

Process	Percentage of Total Cost
Post-Plate Grinding/Finishing	26.22
Set-Up and Masking	19.80
Process Operation Labor	19.49
Materials (maintenance)	12.77
Waste	9.84
Shot Peening	7.47
QA Labor	3.40
Materials (consumed)	0.78
Electricity	0.23
Total	100.00

#### F.3.1.5 Canada's Costs

In 1983, Environment Canada surveyed the Canadian surface finishing industry (Overview of the Canadian Surface Finishing Industry. December 1987. Report EPS 2/SF/1. Environment Canada). Out of a total of 539 shops, 15% reported data on treatment costs. The survey divided treatment costs into three categories. Approximately 32% of respondents reported treatment costs of between \$0 and \$10,000 per year. Another 32% reported treatment costs of between \$10,000 and \$50,000 per year. The remaining 36% reported treatment costs greater than \$50,000 per year (1983 Canadian dollars).